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FERMENTATION AS A SOURCE OF GLYCERINE
WITH CONSIDERATION OF THE
1948-1950 OUTLOOK
and
PRESENT SITUATION

by

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Especially Prepared
for the

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FOREWORD

It has been known for a long time that small quantities of glycerine are regularly produced in the course of normal alcoholic fermentation. During periods of shortage, as in World War I, many scientists studied the possibility of increasing the yields of fermentation glycerine by modifying the conditions under which yeast cells were forced to work. Such efforts led to development of processes that were practicable enough for glycerine production on a considerable scale during periods of special stress but they were not sufficiently economic to compete with glycerine produced during normal times from fats as a by-product of soap manufacture.

However, conditions in chemical industries are always subject to rapid and radical change. Hence, it has been considered wise to make a careful survey of trends in glycerine demand and supply and especially to assay the effects of many newer trends and developments upon the feasibility of industrial glycerine production by fermentation.

Among these newer developments may be listed (a) the growth of synthetic detergents as competitors of soap, (b) the increasing demand for glycerine in the glyptal resin industry, (c) the initiation of synthetic glycerine production from petroleum, (d) the improvement of fermentation glycerine yields and production techniques and (e) the development of dialysis for large-scale separation of water-soluble substances, a technique which promises to facilitate isolation of fermentation glycerine.*

Among the scientists who first studied the modification of alcoholic fermentation for the production of glycerine was Professor Carl Neuberg, then of the University of Berlin. As Research Professor of Chemistry at New York University, Professor Neuberg was given two grants-in-aid by

. . . .

* The last 5 patents attached at the end of this report concern dialysis.

350 ① Sugar fermentation
② refined glycerine
③ glycerine consumption
④ ester gums
⑤ resins
⑥ gaskets ⑦ cork products
⑧ cellulose film ⑩ lipids
⑨ meat casing

the Sugar Research Foundation for
of the problem. In particular he s
stirring upon the speed of ferment

The present report includes
cerine production and consumption,
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a final report of Professor Neuberg's research for the Sugar Research
Foundation.

Robert C. Hockett
Scientific Director
Sugar Research Foundation, Inc.

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The maximum yearly refined glycerine production from domestic crude production cannot exceed 190 million pounds, 100% glycerol basis, or 194.6 million pounds on the basis of market grades, 97.8% glycerol.

The outlook for crude and refined glycerine production is based on the 1948-1950 estimated fat and oil consumption in the manufacture of soaps and fatty acids. A maximum recovery of 88% from total fats and oil consumed to crude would have to be attained. It is doubtful whether an overall recovery beyond this could be achieved economically.

Glycerine, as a by-product of the soap and fatty acid industry, has reached the peak of its economical output. At the present time, the possible supply is below the demand and apparent total disappearance.

Synthetic glycerine, now in commercial production since August,1948, could not have started at a more opportune time. Its presence on the market should stabilize the availability of glycerine at a reasonable price level, which, however, will be about 50% higher than wartime prices. There will be greater possibilities for new and increased uses of glycerine. Glycerine substitutes presently enjoying part of the glycerine market, primarily because of uncertainty of supplies and price fluctuations will lose outlets to this end.

The quality of synthetic glycerine is stated to be better than presently available market U.S.P. glycerine and there is presumably no difference in the toxicity of the natural and synthetic product. By early 1949, this claim will be substantiated or disproved. Present prices for the synthetic are about 25 cents per pound or substantially less than the present price of the natural. Shell is presently promoting intermediates from its synthetic glycerol process and if they can develop the proper conditions, it is estimated marginal flexibility of costs can be reached to the extent that a profitable glycerine market may be enjoyed, competitive to the natural glycerine selling price.

A technico-economic comparison of the Shell synthetic glycerol process versus the soap makers by-product is not possible, since detailed cost particulars of the former are unavailable. Corrosion and other difficulties of such a new operation will probably take some time to be ironed out.

There are 10 natural glycerine refiners with 27 plants distributed throughout the United States. Three refiners do not produce any crude glycerine and account for approximately 7.9% of the total refined glycerine output. Four soap companies refine approximately 88% of the total output of glycerine from natural sources.

Commencing in early 1949 through 1950, it is estimated that the yearly average production of synthetic glycerine from Shell's plant at Houston, Texas, will be 25 million pounds. This would amount to 11.5% of the total natural and synthetic market grade glycerine.

The total market available glycerine, natural and synthetic, in 1948-1950 will be approximately 217 million pounds. Current production of glycols and such higher alcohols, such as sorbitol, mannitol and pentaerythritol will reach a total of 350 million pounds early in 1949, or, 75% more than the output of glycerol. They are also destined to grow further, on account of the greater elasticity in their production and consumption. Total possible output will be below domestic disappearance in 1948-1950, under normal conditions. The balance will be met with synthetic glycerol, as well as higher alcohols and glycols. Glycerol production, even after 1950, is not expected to increase, on account of the increasing encroachment of synthetic detergents on ordinary soap. Capacity for detergents is now 700 million pounds annually and is expected to grow to over one billion pounds by 1950.

While synthetic glycerol will stabilize the price ultimately, it will contribute to keeping the prices relatively high until 1950, because of long-term contracts. While the price will drop from its present heights, it is not expected to go below a level of at least 50% higher than the wartime prices.

The production of glycerine has not been able to keep up with consumption which is constantly increasing. Strangely enough the increase in glycerine consumption can not be entirely traced to increased activity in the alkyd resin field which ordinarily consumes as much as 30 million pounds of glycerine yearly in the preparation of special coating preparations. Actually the expansion of alkyd resin activities has been held up by the shortage of phthalic anhydride, another raw material required. With the newly opened plant of the Barrett Division of the Allied Chemical and Dye Corp. now supplying additional phthalic anhydride, additional amounts of glycerine will be required.

Soap manufacturers have been producing more glycerine this year than in 1947. The question then, of where all this glycerine is going to is a puzzling one. The Glycerine Producers' Association believes that prewar breakdowns of glycerine distribution still apply basically. Probably more glycerine is going into the production of maleic acid (although this use is not too extensive), and into tobacco and cellophane.

Shell's production of synthetic glycerine is the new factor. The tie-in between soap and glycerine has caused glycerine to fluctuate widely in price. Since Shell's output will be about 10-15% of the total domestic production, it will help considerably to stabilize the price of glycerine.

Although glycerine refineries have still capacities of almost 250 million pounds of glycerine per year, their production is limited by the market for and price of their main product, soap.

The fact that Shell has gone into the production of synthetic glycerine does not mean that the prospect for future synthetic glycerine plants is bright. Construction of another synthetic glycerine plant may cost almost twice as much as Shell's plant at the present time.

It therefor seems that the country will be faced with a considerable shortage of glycerine for some considerable time, and that the production of glycerine from alternative sources might be commercially feasible. For this reason, the production of glycerine by the fermentation of molasses or sugar deserves new consideration at the present time.

November 30, 1948

GLYCERINE RESUME

SUMMARY

of

PROPERTIES, USES, CONSUMPTION, SUBSTITUTES,
PRODUCTION (NATURAL AND SYNTHETIC), REFINERS,
PRICES, TARIFFS, IMPORTS,
EXPORTS

* * * * * * * * * * *

IV - GLYCERINE RESUME

A. Properties: Glycerine or glycerol, $CH_2OHCHOHCH_2OH$, a trihydric alcohol, is a clear, colorless, syrupy, sweet liquid. It is very hygroscopic and absorbs moisture, sulfur dioxide, and hydrogen sulfide from the air. It is miscible with water and alcohol but insoluble in benzene, carbon tetrachloride, and chloroform. Pure glycerol has a specific gravity of 1.2653 at 15.5/15.5°C, a boiling point of 290°C. at 760 mm, a vapor pressure of 64 mm. at 100°C. when the total pressure is 760 mm, and a melting point of 17.0°C. but crystallizes slowly on cooling below this temperature.

Chemically, glycerol, as a trihydric alcohol, is capable of forming mono, di, and tri esters and ethers. It can react to form acetals, amines and halodydrins. Acting as a weak acid it forms metallic derivatives. Besides lending itself to numerous varied special reactions, glycerine can be oxidized, reduced, and dehydrated to form many products.

The continual demand and increasing development for further possibilities of glycerine use is dependent upon the numerous physical and chemical properties of this substance. It may act as a humectant or hygroscopic agent, a solvent, a vehicle, a bodying agent, a suspending agent, a lubricant, a heat transmitting material, a pressure transmitting agent, an antifreeze, a softener and plasticizer, a sweetener, a penetrant, an emollient, and a bleaching agent. Then it forms many chemical compounds: namely, such present-day important derivatives as alkyd resins, ester gums, nitro-glycerine, acetins, and long-chain fatty glycerides.

These properties combined with its non-toxicity and stability to oxidation, carry glycerine into a wide diversity of industrial and edible products.

B. Uses: The following tabulation* portrays a list of products and fields of manufacture into which glycerine enters:

Drugs and Pharmaceuticals - See. U.S.P. XIII & N.F. VII Prepn.
Dynamite, Nitroglycerine, and Smokeless Powders
Synthetic Resins and Ester Gum
Rubber Processing
Gaskets and Cork Products
Cellulose Films and Meat Casings
Glassine, Greaseproof, and Vegetable Parchment
Printers' Rollers and Supplies
Textile Processing
Leather Products - Shoes, Harness, Belts, Lining, Skins, Patent Leather, Processing, Leather etc.
Adhesives - "Scotch" Tape, Bookbinding, Labels, Envelopes, Gummed Tapes, Wood and Paper Adhesives, Postage Stamps, Mucilage, Rubber-Casein Adhesives.
Paper other than Glassine and Greaseproof
Beverages, Flavors, Candy and Gum - Wines, Beer, Cordials, Soft Drinks, Chocolates, etc.
Margarine, Shortening, Biscuits, Cakes, Bread, Shredded Cocoanut, Jelly, Mustard, Tobacco

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* Source: "The Fats and Oils Situation", Bureau of Agriculture Economics, U. S. Dep't. of Agriculture--Feb. 1944, FOS84 and Dec.1944, FOS94.

Dentifrices and Toilet Articles - Toothpaste, Creams, Perfumes, etc.
Cleaning Materials - Soaps as milled and bar, Liquid Soap, Lather and Saddle Soap, Rug Paste, Soap, Hand Soaps, Polishes, Cleaners, Synthetic Detergents, and Wetting Agents.
Manufacture of Chemicals - Reagent Chemicals, Mfg. of Acrolein, Mfg. Mono, Di, and Triacetin, Invertase, Hydrogenated Naphthas, Naphthalonate Driers, Reconstructed Oils, Basic Dyes, and misc. Chemicals.
Hydraulic Fluids - Door Closures, Air (and other) Brakes, Vessel Launching, Floor Hinge Liquid, and Recoil Mechanisms.
Insect and Micro-Organism Control - Insecticides, Bactericides, Germicides, Fungicides, Sticky Fly Paper.
Embalming Fluids.
Decorative Articles and Toys - Cemetary Wreaths, Artificial Flowers, Dolls.
Soldering Compounds.
Lubricants - Air Brake Lubricants, Thread Lubrication on Oxygen Cylinders, Die Lubricants, General Lubricants.
Cement Compounds - Litharge-Glycerine Cement, Pipe Joint Cement, Furnace Cement, Transformer Cement, Freight Car Wood Patch, Plastic Caulking Compounds, Rethreading Compounds.
Waxes and Emulsions - Optical Waxes, Emulsifiers, Wax Emulsions, Industrial Protective Creams.
Instrument and Equipment Manufacture - Mercury Action Thermometers, Engine Gauges, Electrical Equipment, Telemotor Systems, Oil Refinery Equipment, and Flexible Metal Hose and Tubing.
Packing Compounds - High Pressure Rod Packings, Mechanical Packings (asbestos), Gasoline Resistant Packings, High Pressure and Temperature Packings.
Laboratory and Research.
Anti-Freeze Fluids - Automatic Sprinkler Systems, Defrosting for Glass, Deicing, and Gasoline and Diesel Engines.
Masking and Shielding Compounds - Paint Spray Shield.
Grinding Compounds - Vitrified Grinding Wheels, Valve Grinding and Lapping, and Artificial Polishing Stones.
Electrolytic fluids - Galvanized Cloth, Lightning Arrestor.
Coolant Fluids - Cutting Solutions for Metal Working, Quenching Fluids for Tools.
Miscellaneous Manufactured Products - Asphalt, Coal Tar Products, Flexible Vulcanized Fibre, Pressure Sensitive Tape, Diaper Liners, Fish Bait, Ceramic and Water Colors, Photographic Products, Fire Retardants, Galvanizing and Plating Preparations, Molding Clay, Graphite Pencil Leads, Artificial Leather, Shoe Lining and Ink.

Miscellaneous Fluids - Anaesthetics, Sealing Fluids, (for centrifugal pumps), Dust-Collecting Liquid, Stencil Correction Fluid and Oxidation and Evaporation Inhibitors.

Besides the above enumerated uses in which glycerine finds application additional uses are always appearing. The uses of glycerine have been presented in this manner since on this same basis consumption of refine grades of glycerine will be examined.

For a detailed summation of glycerine uses the Glycerine Producers' Association (3) have published a booklet showing "1583 ways to use glycerine' The general captions of the numbered uses may be generalized as follows:-

Material Arts and Sciences (3)

Title of Application	Uses Given
1. Air, Conditioning and Refrigeration	1 - 15
2. Adhesives and Pastes	16 - 39
3. Automotive	40 - 66
4. Cements	67 - 74
5. Cleaners and Laundry Aids	75 - 98
6. Electrical	99 - 136
7. Explosives	137 - 139
8. Glass, Ceramics, Abrasives	140 - 187
a) Glass	140 - 162
b) Ceramics and clay products	163 - 179
c) Abrasives	180 - 187
9. Laboratory	188 - 212
10. Leather	213 - 249
11. Lubricants	250 - 286
12. Metals	287 - 323
13. Packaging Materials (other than paper)	324 - 341
14. Paper	342 - 395
15. Photography	396 - 445
16. Plastics and Molding Compositions	446 - 468
17. Printing, Lithography, Inks, etc.	469 - 535
18. Protective Coatings(Paints, varnishes,lacquers & enamels)	536 - 609
19. Rubber	610 - 652
20. Textiles	653 - 727
21. Wood	728 - 747
22. Miscellaneous	748 - 793
23. Agriculture	794 - 830
24. Beverages	831 - 856
25. Chiropody and Podiatry	857 - 880
26. Cleanliness, Sanitation and Personal Hygiene	881 - 903
27. Cosmetics and Toilet Preparations	904 - 997
28. Dentistry	998 -1060

29.	Diagnosis, Laboratory and Clinical	1061 -1087
30.	Drugs and Pharmaceuticals	1088 -1392
31.	Foods	1393 -1478
32.	Perfumes	1479 -1490
33.	Tobacco	1491 -1505
34.	Veterinary Medicine	1506 -1554
35.	Miscellaneous	1555 -1583

A book has been written by Georgia Leffingwell and Milton Lesser (6) covering the uses of glycerine. For a commodity which, from its discovery in 1779, has been essentially a by-product of the soap making industry, there is little doubt of its diversified application.

C. GRADES, STANDARDS, SPECIFICATIONS FOR REFINED GLYCERINE:

Refined glycerine may be purchased in four principal grades:

(1) Chemically pure or U.S.P. - A high quality, water-white glycerine suitable for use in foods, drugs, pharmaceuticals, cosmetics, and anywhere such requirements are desired.

- (a) The normal "C. P. Glycerine" is 95% glycerol and has a sp. gr. of 1.249 at 25/25°C.
- (b) A "Super C. P. Glycerine" also appears as a standard grade having a sp. gr. of 1.257 at 25/25 °C., 98% glycerol.

(2) Dynamite - a Yellow glycerine made for the particular use of explosives - This grade has a sp. gr. of 1.262 at 15.5/15.5°C., 98.7% glycerol.

(3) High Gravity - A pale yellow glycerine made for industrial uses. It has a sp. gr. of 1.262 at 15.5/15.5°C., 98.7% glycerol.

(4) Yellow Distilled - A yellow, slightly reddish, glycerine offered for industrial purposes having a sp. gr. of 1.258 at 15.5/15.5°C., 97% glycerol.

Within these grades manufacturers of refined glycerine also produce glycerine to comply with particular tolerances of customer specifications. Usually such business is taken when at least tank wagons or tank cars are involved.

The U. S. P. XIII covers the requirement for C. P. or U. S. P. glycerine, while all grades of refined glycerine are covered by Federal Specification 0-G-491 available from the Superintendent of Documents, Washington 25, D. C., price 5 cents.

D. PACKING, SHIPPING, STORAGE: Refined glycerine comes in different containers. For U. S. P. or C. P. glycerine, the usual containers are 1, 5, and 10 pound bottles; 10 and 50 pound tins; 550 pound drums; tank wagons 20-40,000 pounds; and tank cars 60-80,000 pounds. The usual containers for shipping the other grades are 550 and 1100 pound drums, tanks wagons and tank cars.

Facts pertaining to ocean shipping containers and storage may be found in "Modern Ship Stowage" a 719 page bulletin, Industrial Series No. 1, 1942, issued by the Bureau of Foreign and Domestic Commerce, U. S. Department of Commerce, available from the Superintendent of Documents, Washington 25, D. C., for $1.50.

In shipment or stowage of glycerine, which is hygroscopic, containers should be kept tightly closed to prevent dilution.(7).

E. CONSUMPTION OF REFINED GLYCERINE (Trend Outlook) in U.S.A.:

Table I shows the consumption, allocations, and estimated consumption given by class of use. Incorporated into this table is the writer's estimated grade of glycerine consumed and allocated during the indicated periods. The writer's outlook or estimated average yearly consumption for 1948 - 1950 is also shown.

Table II shows the breakdown of "Miscellaneous" use given in Table I. The data appeared in the December 1944 issue of the Fats and Oils Situation as a supplement to the February article. The first summation of uses followed the governmental pattern of classification of glycerine by use. One can now evaluate the consumption of glycerine in each class of the products its application enters.

The consumptions for 1940 - 1941 inclusive were for peacetime years. The change during war years may be noted by comparing 1943 allocations with 1940 - 1941 consumption figures.

In 1943, despite drastic curtailment in the civilian use of glycerine, as in beverages, flavors, confectioneries, margarin, shortening, edibles in general, tobacco, and toilet articles, the consumption compared with peacetime years 1940 - 1941, and most of 1942. Approximately 29 million pounds of C. P. grade glycerine was made unavailable for civilian use. The tobacco field alone was allocated 17.5 million pounds of C.P. glycerine less than in either 1940 or 1941. This condition was brought about from the increased use of glycerine to meet the war time needs for dynamite, nitroglycerine, protective coatings and other essential war requirements.

In February 1944 (9) the estimated consumption for 1944 was shown as 199 million pounds of refined glycerine products. On January 1, 1944, the total glycerine inventory was 81 million pounds with an expected 195 millions to be produced during 1944. The estimated 1944 consumption was also based on the allowed glycerine use under Food Distribution Order 34, Amendment 2, effective January 1, 1944 which removed glycerine for specific allocation. Most civilian uses of lesser essentiality under this order were limited to the quantity of glycerine used in 1940. It may be recalled that the War Food Order 34 was suspended in March 1944 and then was revoked on May 13, 1944, due to an increased rate of glycerine production and with a decrease in lend-lease requirements.

C. W. Lenth, one of the co-authors of the government GOS article (9), later in an article on "Glycerine Outlook" (11) estimated that a steady requirement of more than 185 million pounds of glycerine may be counted on in the post war years. His estimated consumption for the post war years is shown in Table I.

From a tabulation of apparent glycerine disappearance in the United States, 1919 - 1947, Table IV, the apparent total consumption of glycerine (100%) basis in U.S. A. from 1939 to the present date may be calculated as shown in Table V.

The accessible facts were examined and the yearly consumption during 1947 - 1950 was estimated. The breakdown of the individual classified uses accounting for this consumption is shown below. It will be noted that the important figures of 1940 - 1941 (9) were essentially the basis while Lenth's (11) outlook was given due recognition when in accord with estimated present trends.

TABLE II

CONSUMPTION OF GLYCERINE BY CLASSES OF PRODUCTS
BREAKDOWN OF "MISCELLANEOUS" USE IN TABLE I

Use (a) (d)	(b) Est. Grade	1940 1000#-	 %(c)	1941 1000#	 %(c)
leaning materials	C. P.	1,074	0.77	1,589	0.91
anufacture of Chemicals	C. P.	726	0.52	1,408	0.81
ydraulic fluids	C. P.	137	0.10	140	0.08
nsect & Microorganism Control	C. P.	132	0.09	187	0.11
mbalming Fluids	C. P.	121	0.09	146	0.08
Decorative Articles & Toys	C. P.	99	0.07	114	0.07
Soldering Compounds	H. G.	59	0.04	64	0.04
Lubricants	H. G.	55	0.04	107	0.06
Cement Compounds	H. G.	53	0.04	103	0.06
Waxes & Emulsions	C. P.	50	0.03	76	0.04
Instrument & Equipment Manufacture	C. P.	46	0.03	46	0.03
Packing Compounds	C. P.	32	0.02	50	0.03
Laboratory & Research	C. P.	20	0.01	15	0.01
Antifreeze Fluids	C. P.	17	0.01	35	0.02
Masking and Shielding Compounds	C. P.	15	0.01	29	0.01
Grinding Compounds	C. P.	14	0.01	20	0.01
Electrolytic Fluids	C. P.	4	-	4	-
Coolant Fluids	H. G.	2	-	12	0.01
Miscellaneous Manufactured Products	30% H. G. & 70% U.P.	857	0.61	1,108	0.64
Miscellaneous Compounds	C. P.	15	0.01	14	0.01
Miscellaneous Fluids	C. P.	4	-	6	-
Unidentified	C. P.	354	0.25	995	0.57
Total for Miscellaneous in Table		3,886	2.8(3)	6,268	3.6(3)

(a) "Fats and Oil Situation", December 1944, Bureau of Agricultural Economics, U. S. Dep't. of Agriculture

(b) (c) - Same as (b) & (c) under Table I - -

(d) See Uses in this article for clearer breakdown of products involved - Page 13

TABLE III

GLYCERINE: APPARENT DOMESTIC DISAPPEARANCE CONSUMPTION, SHIPMENTS AND ALLOCATIONS, 1940-1944

Item	1940	1941	1942	1943					1944
				First Quarter	Second Quarter	Third Quarter	Fourth Quarter	Total	Estimated
	1000#	1000#	1000#	1000#	1000#	1000#	1000#	1000#	1000#
	Disappearance, Allocations , and Consumption or Shipments								
Apparent Domestic Disappearance	151,805	206,578	153,369	28,158	30,310	29,570	43,523	131,561	- -
Total quantity specifically allocated under 100-34	-	-	-	33,542	35,626	35,380	56,799	161,347	- -
Consumption or shipments	140,359	175,135	166,350	27,394	30,537	29,897	45,103	13,931	199,150
Small orders and resale	14,309	18,022	7,755	2,717	2,621	2,129	2,308	9,775	
Shipments against specific allocations	-	-	-	24,677	27,916	27,768	42,795	123,156	
Percentage of specific allocations taken				73.6	78.4	78.5	75.3	76.3	

TABLE IV

GLYCERINE, CRUDE, 80 PERCENT BASIS: PRODUCTION, TRADE, STOCKS DECEMBER 31, AND APPARENT DISAPPEARANCE. UNITED STATES

1919-1947

Year	Factory Production	Imports for Consumption	Exports	Net imports or net exports(-)	Stocks Dec.31	Apparent Disappearance
	1000#	1000#	1000#	1000#	1000#	1000#
1919	61,793	3,861	4,707	846	14,050	60,947
1920	54,688	29,004	2,069	26,935	22,825	72,848
1921	63,947	3,400	2,844	556	26,661	60,667
1922	85,337	3,801	3,409	392	25,894	86,496
1923	99,579	15,266	2,099	13,167	25,955	112,685
1924	95,154	16,265	1,681	14,584	26,294	109,399
1925	103,407	21,768	1,624	20,114	15,464	134,381
1926	116,369	40,970	912	40,058	26,214	145,677
1927	128,209	25,158	823	24,335	45,648	133,110
1928	130,499	10,216	2,437	7,779	39,558	144,368
1929	140,080	21,444	1,631	19,813	33,331	166,120
1930	138,675	14,987	722	14,265	32,350	153,921
1931	140,002	12,541	390	12,151	43,034	141,469
1932	133,919	8,258	309	7,949	55,627	129,275
1933	119,812	9,873	1)	9,873	30,246	155,066
1934	153,115	17,793	1)	17,793	41,228	159,926
1935	141,185	8,305	3,982	4,323	43,003	143,733
1936	154,096	15,372	1,361	14,011	38,980	172,130
1937	169,039	22,672	1,633	21,039	70,100	158,958
1938	162,120	16,243	4,449	11,794	97,086	146,928
1939	184,476	11,392	8,786	2,606	88,611	195,557
1940	197,320	9,462	15,580	6,118	90,150	189,663
1941	244,104	9,156	11,982	2,826	75,136	255,992
1942	221,794	6,105	40,798	34,693	70,824	191,713
1943	214,916	10,275	30,716	20,441	101,142	161,157
1944	249,792	6,084	11,384	5,300	109,601	236,033
1945	215,562	9,596	9,496	100	57,150	268,113
1946	196,029	25,088	817	24,271	53,369	224,081
1947	259,710	3,830	5,335	-1,505	60,728	250,846
1948 (est.)	247,000	- -	- -	- -	55,000	253,000

Compiled as follows:
Factory production and stocks, Bureau of the Census, Animal and Vegetable Fats & Oils. Stocks are "crude, 80 percent basis," plus "dynamite" and "chemically pure" converted to crude basis by multiplying by 0.98 and 0.95 respectively and dividing by 0.80. Beginning 1943, production and stocks reported on 100 percent basis; divided by 0.80 to convert to crude basis.
Trade figures, Bureau of the Census, Foreign Commerce and Navigation of the United States. Imports consist of both crude and refined glycerine; refined converted to crude basis by multiplying by 0.98 and dividing by 0.80. Exports 1919-39 are not designated as crude or refined, but apparently are made up largely of refined with the estimated average glycerine content of 95 percent; converted to crude basis by multiplying by 0.95 and dividing by 0.80. Beginning 1940, reported on 100 percent basis, divided by 0.80 to convert to crude basis.

Source: U. S. Dep't. of Agriculture

TABLE V

APPARENT TOTAL CONSUMPTION OF GLYCERINE IN U. S. A. (in 1000 lbs.)

YEAR	Apparent Consumption (a) 80%	Apparent Consumption 100%	Average Since 1939 100%	Average Since 1942 100%	Consu Since 10
1939	195,557	156,446	156,446		
1940	189,663	151,730	154,088		
1941	255,992	204,790	170,989		
1942	191,713	153,370	166,584	153,370	
1943	164,157	131,326	159,532	142,348	
1944	236,033	188,826	164,414	157,841	188,
1945	268,113	214,490	171,568	172,004	201,
1946	224,081	179,265	172,530	173,455	194,
1947	250,846	200,677	175,658	177,992	195,
1948 (est.)	253,000	202,400	178,000	181,000	197,

(a) Source Table IV. This table accounts for net imports (+) or net exports (-), thus apparent consumption in U. S. A.

The average yearly apparent consumption since 1944 has been 197 million pounds. This apparent disappearance is based on both crude and refined glycerine, thus the 100% glycerol basis figure is comparable on a weight basis to market grade glycerine when allowing for 96 - 98% yields from crude to a refined market grade glycerine at an average glycerol content of 97 - 98%.

Pharmaceuticals and Drugs: Only a slight increase in consumption may be expected over the 1941 level, this being based on the increase in population and activity in this field. Greater use could be expected but some substitutes for glycerine in this class of product will apparently enjoy a permanent market. It will be assumed that approximately 12 million pounds will be consumed.

Dynamite and Nitroglycerine - There is a constant demand for dynamite in reconstruction, road building, mining, etc. Although the military requirements are now non-existent, which were included in the 1941 and 1942 consumption figure, the activity in the field is great enough to reach a high level of dynamite production. A consumption between 1941 and 1942 levels may be expected or, about 33 million pounds. Preparedness for another conflict may increase this substantially.

Resins and Ester Gums - In 1942, the production of phthalic anhydride was 95 million pounds and in 1943 a level of 113 million pounds (12) was reached. Presently the average monthly production is 11.4 million pounds or about 137 million pounds per year. There are indications that phthalic anhydride production will probably reach 170 million pounds before 1950. By a new development (27), 8 million pounds a year of phthalic anhydride is being produced by one plant in California by the oxidation of o-xylene from petroleum.

During the recent war on account of military requirements of phthalic anhydride for insect repellents, plasticizers and explosives, together with restriction on the use of oil, WFO - 42 a, the alkyd resins field was more or less cut short of further development. In 1935, the alkyd resin production was 34 million pounds requiring approximately 5.0

million pounds of glycerine (13). By 1939, the production increased to 76.5 million pounds with a consumption of 11 million pounds. In 1943, a production of 154 million pounds of alkyd resins was reached, requiring 35 million pounds of glycerine as reported by Lenth (14). This level may be expected to continue at 35 million pounds since preference for protective coatings on automobiles, washing machines, refrigerators, etc., is still in favor of alkyd resins.

Ester gums production consumed 6.1 million pounds of glycerine in 1940 and 10.5 million pounds in 1941. The consumption increased during 1944 on account of the shortage of alkyd resins. It is believed (14) that as the alkyd resins become available, ester gum production will drop so as to consume 10 million pounds of glycerine yearly.

The total glycerine consumed yearly by resins and esters gums between 1947 - 1950 is estimated to continue at 45 million pounds.

Rubber Processing - The amount of glycerine used in this field has been fairly constant and is expected to continue at an average yearly rate of 1.5 million pounds of glycerine.

Gaskets and Cork Products - During 1941 and 1942 there was an increase of over 2 million pounds of glycerine consumption primarily due to new uses which is at least expected to be retained with possibly an increase for the yearly average in 1947 to 1950. The usage here is estimated at 10 million pounds yearly.

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H. 2,388,840

I. 2,414,838

J. 2,416,745

K. 2,361,000

L. 2,386,381

M. 2,411,238

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I. PREFACE

This survey was undertaken in order to evaluate the present glycerine situation and the possibility of producing glycerine by fermentation methods, especially now that synthetic glycerol has made its debut in the United States market. From the data collected, it is believed that a reliable estimate of the present situation and the 1948 to 1950 inclusive outlook was made possible.

In addition to the conclusions, the reader is referred to the charts and tables shown in the summary of this survey. The collected factual information should prove of interest. This report was designed as a ready reference. Sources of all obtained data are immediately given or indicated by reference to the bibliography.

Despite the additional capacity of synthetic glycerine, the demand for it is increasing faster than the supply, indicating some long term opportunities for fermentation glycerine.

II - MANUFACTURE OF GLYCERINE BY SUGAR FERMENTATION

When fermentable sugars are acted upon by yeast under normal acid condition, ethanol, carbon dioxide, and small quantities of glycerol and acetic acid are produced. The small quantity of glycerine produced makes this process commercially impossible for the production of glycerine alone.

The two general methods that have been suggested for the production of glycerine by fermentation are the sulfite fixation process, and the alkaline fermentation process. In the last few years new developments have occurred which make such processes more commercially feasible.

In the sulfite fixation method, a soluble sulfite is added to the fermentation mixture in sufficient quantity to produce fixation of acetaldehyde which is formed in the fermentation. This shifts the equilibrium of the reaction and increases the quantity of glycerine formed.

In the alkaline fermentation process, the fermentation is carried out in a medium made alkaline by the addition of alkaline salts or bases.

Unfortunately both of these processes must be carried out in alkaline media which are unfavorable to the growth and action of yeasts.

Moreover, the large quantities of soluble salts which remain in the medium after the reaction make the separation of glycerine difficult. Some experimenters have attempted to use gaseous sulfur dioxide in the sulfite fixation process, but the amounts required are toxic to the yeast cells. A very great amount of salts and alkalies is required in the processes first used by the Germans in the first World War. For example, the fermentation of 100 tons of sugar by the Connstein and Ludecke process required the addition of almost 30 tons of salts, and the fermentation of the same amount of sugar by the alkaline fermentation soda-ash process of Eoff required the addition of the same amounts of salts. The costs of the added salts alone are sufficient to make these processes used in the past impractical.

As pointed out previously, alkaline mashes retard the growth of the yeast cells. Furthermore, immediately after the addition of the alkaline materials to the mash, the yeast cells are rendered inactive for two to three hour periods. During this time, it is relatively simple for the mash to become infected with contaminating micro-organisms.

As a result of these objections the use of an acid medium was suggested. However, when this was first tried, low glycerol yields of only 3% to 4% were obtained (see Connstein and Ludecke: U. S. Patent 1,511,754).*

A practical process involving the use of an acid medium has been proposed in U. S. Patent 2;3$1,052* (August 7, 1945), assigned to U. S. Industrial Chemicals, Inc.

In general, the patented process is carried out in the following manner. The yeast crop is grown by aeration in a dilute sugar mash, and after 12 to 24 hours, sufficient molasses is added to bring the sugar content up to 15 to 20 grams per 100 cc.

Fermentation sets in promptly, and aqua ammonia is added until the pH of the mash is between 6.0 and 7.0. Ammonium salts may also be used for this purpose, but aqua ammonia is preferred. When distilling occurs the pH is adjusted to 6.0, at which point the ammonia is not volatile. During fermentation the acidity can be adjusted within the required limits by the addition of hydrated lime.

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* A copy of this patent may be found at the end of this report.

By this method the yield of glycerine obtained is greatly increased. It is suggested that the two stage glycerol operation described by Hildebrandt and Erb (U. S. Patent 2,169,245 *-August 15,1939) be employed in carrying out the fermentation.

Another improved process developed by Schade and Farber (U. S. Patent 2,414,838*- January 28,1947 - assigned to the Overly Bio-Chemical Research Foundation), involves fermentation in the presence of magnesium carbonate to increase the yield.

In addition, reaction products more volatile than water are removed during the course of the reaction. A neutral gas such as air is also bubbled through the fermenting solution to mechanically aid in the removal of carbon dioxide and similar volatile gaseous products. The pH is maintained between 7 and 8. The fermentation of a batch is completed in about one day. The amount of glycerine produced amounts to about 26% of the sugar used for fermentation.

In another method proposed by Fulmer, Underkofler, and Hickey (U. S. Patent 2,388,840*- November 13,1945 and U. S. Patent 2,416,745*- March 4, 1947 - both assigned to the Iowa State College Research Foundation), acetaldehyde is fixed by reagents which can readily be removed after the fermentation is complete by filtration or volatilization. The glycerine can then be more easily separated from the smaller amounts of salts left in solution. The fermentation reaction is permitted to proceed in the presence of ammonium salts in acid medium, and sulfites which bind the acetaldehyde formed. The maintenance of a pH between 6 and 7 prevents the formation of free ammonia which is toxic to yeast.

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* A copy of this patent may be found at the end of this report.

Fermentation is completed in 18 to 72 hours. In separating glycerine, the mixture is first made alkaline, and ammonia, ethanol, and acetaldehyde distilled off. The lime used to make the mixture alkaline is removed by precipitation as the carbonate.

The resulting filtrate containing the glycerine can be purified by vacuum distillation or through the use of a selective solvent.

An account of experimental work recently conducted on the glycerine fermentation process is detailed in **Section V.** This account was prepared especially for the Sugar Research Foundation by Dr. Carl Neuberg as a report upon Foundation Project No. 5.

III - THE GLYCERINE OUTLOOK

1948-1950 Inclusive, Based on Summary of Present Situation

Summary of Conclusions

Yearly consumption of market grade glycerine during 1948 - 1950 will be in the neighborhood of 192 million pounds in the United States. The class of products creating this demand indicate 45% of this consumption will be C.P. Glycerine and 55% Dynamite, High Gravity and Yellow Distilled.

Primarily on account of fat and oil shortages abroad, the United States has become a net exporter. Three to ten million pounds may be exported yearly in 1948-1950, depending upon domestic supply.

Total disappearance of market grade glycerine from the United States on this basis may be estimated as from 195 - 202 million pounds yearly during 1948 - 1950.

In 1948, the crude production will approximate 203 million pounds while the refined glycerine 197 million pounds, both on 100% glycerol basis. This output cannot be expected to be maintained in the immediate subsequent years, chiefly on account of the rapidly increasing developments in the synthetic detergent field and continued fat shortages.

During 1948-1950, the yearly average fat and oil consumption in the soap industry is estimated at 1,728 million pounds and 300 million pounds of fats and oils are expected to be consumed in the fatty acid industry. This takes into consideration an increase in population and further development of synthetic detergents which are essentially derived from petroleum hydrocarbons.

The maximum yearly crude glycerine production that could be expected is 195.6 million pounds, 100% glycerol basis. Approximately 84% will be produced as soap lye crude and 18% as saponification crude.

Cellulose Film and Meat Casings - Some substitutes have made inroads in such products especially those designed for specific purposes. The production of cellophane and meat casings over the 1941 level is expected to be exceeded with a probable yearly consumption of 21 million pounds during 1948 through 1950.

Glassine, Greaseproof and Vegetable Parchment Papers - There have been developments in this class of products with an increase in production facilities. For the present, it is believed that the estimated consumption of Table I for 1944 is being reached and will continue in the neighborhood of 3 million pound glycerine usage.

Printers' Rollers and Supplies - It is estimated that range of glycerine consumption here will be approximately 5.5 million pounds yearly which is a slight increase over the 1942 consumption.

Textile Processing - The trends in processing practices in this industry being unknown to the author, estimated glycerine consumption is placed at the current figure of 2.5 million pounds as probable.

Leather Processing - There have been some new developments in leather processing. However, there are not any apparent indications that the average consumption of glycerine during 1940 - 1942 of a conservative 0.4 million pounds will be exceeded. Nevertheless, 0.5 million pounds is still a safe estimate.

Adhesives - Glycerine substitutes have apparently absorbed most of any increased production in adhesives over 1940-1942 levels. It is believed that approximately 2.5 million pounds of glycerine will be used in this field.

Paper Products other than Glassine and Greaseproof - There have been many new developments in this field and it is probable that 2 million pounds of glycerine will be consumed yearly, 0.5 million pounds over the 1942 level of consumption.

Beverages, Flavors, Candy and Gum - Because of curtailment of glycerine use during the war, it did not enjoy any additional consumption in increased production of such products. However, it is believed glycerine is gradually entering the war developed products. 2.5 million pounds may be safely assumed, consumed in these products. This is just about equivalent to the 1941 consumption.

Margarine, Shortening and Other Edible Products - The margarine market has not dropped off since the end of hostilities chiefly on account of the high price of butter. Regardless, margarine will enjoy a greater market than in pre-war years. The production of shortening has also increased. Developments in edible products particularly the freezing of foods are expected to have increased substantially. It is estimated that a 7 million pound yearly glycerine usage will be averaged during 1947 - 1950. The average yearly consumption in 1940 - 1941 was 3.5 million pounds; thus, this is a 100% increase.

Tobacco Products - In 1943, the curtailment of glycerine used in the tobacco industry amounted to 17.5 million pounds less than the peacetime years of 1940 and 1941 when the consumption of glycerine was 25 million pounds yearly. This was a tremendous reduction and was ideal for glycerine substitutes to make serious inroads into this market.

Bland apple syrup was found to be a very satisfactory substitute, it being approximately 85% as hygroscopic as glycerine, non-toxic, and with no foreign taste. An average yearly glycerine consumption of 20 million pounds as in 1943 would not be a low estimate for 1948 - 1950 and, in fact is considered low in view of the increase in cigarette production.

Dentifrices and Toilet Articles - Glycerine substitutes have entered this field during the war years and will retain part of their penetration in to this market. However, there has been some increased production in these products. A yearly consumption equivalent to peace years 1940 - 1941 of 10 million pounds is a fair estimate.

Miscellaneous - As indicated previously, hundreds of diversified uses fall in this category. From 1940 to 1941 there was an increase from 3.9 million pounds to 6.3 million pounds and in 1942, 7.9 million pounds of glycerine were consumed. Part of this increased usage over 1940 was accounted for by war requirements. Table II shows an interesting trend of consumption in this field. Manufacture of chemicals, cleaning materials, unidentified, insect control, lubricants, and cement compounds accounted for 85% of the 1941 increase over 1940. It is reasonable to assume that the 1941 level of consumption indicated industrial developments. An estimated increase in population of 6% by 1950, further industrial developments allowing for inroads by glycerine substitutes, and the fact that in this classification new outlets originate, consumption should still be over this 1941 level. An average of the 1942 consumption and 1943 allocations would be a conservative yearly consumption of 9 million pounds of glycerine during 1948 - 1950.

Unclassified Small Orders (Table I,j) - There are many untraceable small orders that account for a portion of yearly total consumption of glycerine. The War Food Administration (9) (10) reported disappearance by class of uses, accounting for more than 95% of the apparent total consumption. Perhaps it should be mentioned that these small orders may find their way into the classified or miscellaneous use fields. Thus it was deemed best to treat this consumption separately and it is so indicated in Table I.

Up to this usage, the total consumption sums to 187 million pounds. It is estimated this figure accounts for 97.5% of the apparent total usage. Hence, it follows that a yearly consumption of 5 million pounds may be assumed by unclassified small orders.

From the above as shown in Table I, the derived average yearly total consumption of glycerine for 1948 - 1950 may safely be assumed to be in the neighborhood of 192 million pounds in the United States. This outlook is further substantiated when Table V is examined where it may be noted that since 1944 the average indicated consumption derived from apparent disappearance is 193 million pounds on a 100% glycerol basis.

Figure 1 shows the average yearly estimated consumption by classes of products during 1948 - 1950.

F. GLYCERINE SUBSTITUTES: Lacking efficient processes for the synthesis of glycerine as was apparent in the first World War, the British and German chemists made great strides in the manufacture of glycerine by fermentation, and production of substitutes (16) was also resorted to. Most of the glycerine substitutes up to 1923 were advertised for use in pharmaceuticals, toilet preparations, and miscellaneous external applications. These were generally found to be poor substitutes for glycerine, enjoying only short lived markets to this end. During World War II, glycols were used in Germany for cellophane plasticizers, primarily on account of glycerine shortages.

Shortly before this country entered the recent world conflict, substitutes began making inroads into the glycerine consuming market. During these hostilities, mostly on account of curtailment of civilian glycerine use, these compounds flourished. The extent to which such substitutes have made successful inroads is still hard to determine. In any event, the current status of glycerine situation generously favors the substitutes. Yet in many civilian applications the inrush of substitutes has already dropped.

Of the early substitutes that appeared (16), those for internal use were comparatively simple mixture of sugars occasionally adulterated with aqueous inorganic salt solutions to resemble the consistency of glycerine. Alkaline lactates under the name of Neuberg and Reinfurth "per und perka-glycerin" were believed used by the Central Armies for medical purposes. A boiled and filtered 3% Irish Moss solution to which 5% glucose was added also found medicinal use.

Some of the earlier external type glycerine substitutes consisted of a mixture of tri-cresyl-phosphate, dicresyl, and tricresyl-carbonate (17). Other mixtures contained phenyl and cresyl esters of phosphoric acid (18). Claims appeared for magnesium butyrate and magnesium chloride dissolved in a minimum of alcohol and glycerine for technical purposes in pharmaceutical and cosmetic products (19). A mixture of zinc chloride and lactose in propylene glycol was a claimed substitute (20). An 80% solution of sodium lactate was proposed as a softener of leather. Dipropenyl glycol and butylene glycol were substitutes. An economical substitute consisted of a mixture of betain hydrochloride, with salts, such as calcium carbonate, magnesium carbonate, or magnesium oxide (21).

During World War II, Germany produced a mixture of glycerine, polyglycerols, and glycols by hydrogenolysis of carbohydrates (4). Neither this mixture nor glycerol products obtained by fermentation have been found suitable for nitration. This is being currently investigated from the technical-economic point of view by the Sugar Research Foundation.

So far, ethylene glycol has been the principle substitute for glycerol in some industrial uses (23). The Food and Drug Administration does not permit it in cosmetics, foods, beverages or medicines because of its alleged toxicity. Nevertheless, ethylene glycol has established itself as a permanent anti-freeze primarily under the trade marked product "Prestone" (22) and other trade names. As a point of interest, the present production of ethylene glycol is approximately 250 million pounds per year (15). In this same class propylene glycol is finding application and like ethylene glycol but in a lesser degree is undesirable for human use. These restrictions should include its use in cellophane.

Sugars have always been substitutes for glycerine, not for the fact that glycerine is sweeter than sugars, but for the advantages that glycerine offers in blending moist keeping properties. Bland apple syrup (24) currently is a satisfactory substitute for glycerol because of its high levulose content especially in tobacco products, but it has also made inroads in ice cream, pastry, candy, paper, textile processing, pharmaceuticals, cosmetics, and sugar-curing of hams. This syrup contains three sugars - levulose, dextrose, and sucrose, which constitute about 65%

of the syrup. The non-sugar solids of the apple juice consist of small amounts of malic acid, tannin, pectin, soluble salts, coloring matter, and various nitrogeneous materials. It is 80-85% as hygroscopic as glycerine, non-toxic, and imparts no foreign taste.

By its use as an intermediate in the production of explosives, pentaerythritol was introduced before World War II and its growth was greatly accelerated since (22). Its peacetime outlook appears very promising in the manufacture of alkyd resins and extensive uses exist for it in up-grading drying oils in the paint industry. The Imperial Chemical Industries, Ltd. is converting an explosive factory for the production of pentaerythritol (25). The Heyden Chemical Co. and The Hercules Powder Co. are the main producers in this country.

Polyethylene and polypropylene glycols have grown in importance in the last five years (22). The lower polyethylene glycols are clear hygroscopic liquids with much lower volatility than glycerine and present themselves as substitutes. The higher series are solid compounds having the usual characteristics of being waxlike, but completely watersoluble. These compounds have already established themselves in the pharmaceutical industry.

The synthetic aliphatic industry has grown tremendously in the past twenty years. The infiltration of new chemicals into the glycerine market should be expected, but the extent to which substitutes make inroads will depend upon the stability of a reasonable glycerine price and its availability. As far as can be determined, there is no satisfactory glycerine substitute.

Prior to World War II, polyhydric alcohols like sorbitol and mannitol appeared on the commercial market. Mannitol was in crystalline form while sorbitol was sold commercially in an 85% solution, it being promoted as a glycerine substitute. Recently (26) the Atlas Powder Company has been advertising two commercial grades of sorbitol:

Sorbo - A highly refined, 70% solution of D-sorbitol, water-white, sweet taste, and no odor.

Arlex - A grade of sorbitol containing closely related polyhydric materials which made it non-crystallizing.

These products are being promoted as conditioning agents and humectants in cosmetics, flexible glues, leather, paper, gelatin, chewing gum, candy, tobacco, polishes, yeast, soft drinks, pharmaceuticals, and printers' rollers; also as manufacturing ingredients in drying oils, hard resins, alkyds, esters, ethers and plasterizer. There is no question but sorbitol presents itself as a glycerine substitute with this list of suggested uses.

G. METHODS OF PRODUCTION OF GLYCERINE: Presently with the expectation that 15% of our glycerine will be synthetic in the near future approximately 84% of the glycerine produced in the United States is the result of the manufacture of soap, while the balance of 16% results from other saponification or hydrolysis of fats and oils. Since its isolation, glycerine production has depended on these saponifications, in the first case saponifying oils and fats with caustic soda to yield salts of fatty acids and glycerine and in the other hydrolyzing fats and oils under varying conditions, the more important of which are by steam pressure with or without catalyst, at ordinary pressures with a special catalyst (Twitchell process), and by the action of enzymes. Thus, glycerine is essentially a by-product of the manufacture of soap and fatty acids.

During World War I, Germany produced 13,000 tons per year of glycerine made by fermentation from beet sugar. Many attempts have been made and are being made to perfect the fermentation production of glycerine especially during any war emergency or when the market is inviting. In spite of the many different fermentation processes that have been developed, most have been shortlived or completely abandoned on a commercial basis. What further progress will be made in the fermentation process of sugars to refined glycerine products remains to be seen. High prices for glycerine, coupled with low molasses prices (since most of our industrial alcohol will be synthetic) and an unused fermentation capacity (such as, for example, by U.S. Industrial Chemical Co.) should induce many to consider fermentation.

A description of the manufacture of "glycerogen" by the continuous hydrogenolysis of invert sugar by I. G. Farbenindustrie in Germany is contained in a report which can be purchased from the Office of Technical Services, Department of Commerce.

"Glycerogen" is described as a glycerol substitute consisting of glycols, glycerol, erythritol, and other compounds. The report states that the process "is of considerable technical interest in that it represents the only large scale application of continuous hydrogenolysis of sugars at elevated temperatures and pressures."

The 51-page report is based on investigations made by the late Dr. R. Max Goepp, Jr., an organic chemist formerly employed by the Atlas Powder Co. Wilmington, Del.

The glycerol substitute "glycerogen" consists of about 35 percent glycerol, 35 percent glycols, and 25-28 percent hexitol, the report states. The I. G. Farben plant at Hoechst produced about 250 tons of it a month, using a high pressure continuous hydrogenolysis process originally developed at the IGF Ludwigshafen plant. The monthly output was never increased because the product did not have sufficient commercial value.

The development of glycerol substitutes in Germany was approached from many directions, according to the report. For example, the synthetic fats program called for chemically pure glycerol for which the "Oppau process" involving propylene chlorination and hydrogenolysis was developed. For alkyd resins, the functionally related trimethylol propane process achieved considerable success. However, for the numerous softening and conditioning uses of glycerol in tobacco, cellulose films, cosmetics and pharmaceuticals, the chemical identity of the product with glycerol was irrelevant so long as the substitute had the proper viscosity, taste, lack of color, and was non-toxic.

Several years of experimentation with small scale equipment showed that invert sugar could be cracked to give mixtures averaging 35 percent each of glycerol and glycols (largely propylene glycol), and 25-28 percent of a non-volatile, six-carbon residue. The material was colorless, reasonably sweet in taste, non-toxic, and resembled glycerol in viscosity. In 1937 the decision was made to adopt long, unstirred, liquid phase reactors, agitated by circulated hydrogen. In 1938 the present plant at Hoeschst was constructed for a 250 ton per month production level.

Commercially, however, glycerogen has never been regarded as more than a substitute for glycerol. Considerable difficulty has been experienced in its manufacture, particularly in learning how to prevent corrosion and stoppage of the reactors by the suspended catalyst and how to accomplish pressure release without damage to pumps. Of technical interest, however, is the fact that the process applies continuous catalytic hydrogenolysis to sugar at a temperature of 200 degrees C. and a pressure of 325 atm. "In view of the general applicability of the techniques involved, it has seemed worth while to study the glycerogen process in greater detail than that hitherto reported", the author states.

Dr. Goepp's report (PB-30393, The I.G. Hoechst glycerogen process) discusses the chemistry of the process in outline, the direction of flow and type of equipment used in inversion, reduction and cracking, recovery, general layout of the Hoechst plant, catalyst preparation, production and cost data, and the composition, properties and uses of glycerogen. Nineteen drawings and tables are included illustrating inversion, make up, reduction and cracking, recovery, separator valves, reducing, pressure release and angle-stop valves, and other details of the operation. The mimeographed report sells for $1.50. This report is now being evaluated from the technical-economic point of view by The Sugar Research Foundation.

Other reports on German Technology related to the subject are:

PB-206 (Miscellaneous chemicals, I. G. Farbenindustrie A. G., Hoeschst am Main, by R. E. Richardson, J. G. Kern, R. L. Murray, and R. W. Sudhoff; mimeographed, 25 cents, 48-pages.)

PB-15158 (The paint, varnish, and lacquer industry in Germany, by H. O. Farr, mimeographed, $1.75; 66 pages).

PB-2423 (Glycerogen, a substitute for glycerol and synthetic glycerine; by R. E. Richardson; photostat, $3; microfilm, 50 cents; 35 pages).

Orders for reports should be addressed to the Office of Technical Services, Department of Commerce, Washington 25, D. C., and should be accompanied by check or money order, payable to the Treasurer of the United States.

In August,1948, the Shell Chemical Corporation began the commercial production of synthetic glycerine from propylene. This synthetic product is stated to at least equal the natural product. After ironing out some initial difficulties, the plant should go into full scale production.

GLYCERINE PRODUCTION FROM SAPONIFICATION OF FATS AND OILS: As a by-product of the manufacture of soap and fatty acids, the available supply of crude glycerine is dependent upon the principle raw materials entering into the production of these products. It follows, therefore, that the amount of low-priced or by-product oils consumed in these allied industries will require consideration.

Crude glycerine is solely used as the raw material for the production of refined glycerine. The crude glycerine comes in two grades, soap lye, and saponification crude:

	Soap Lye Crude Average	Saponification Crude Average
Net Glycerol	80.0%	88.0%
Organic Residue	2.5%	1.5%
Ash	10.5%	2.0%
Moisture	7.0%	8.5%

The bulk of the domestic production of crude glycerine is accounted for by three large soap companies (Proctor & Gamble, Lever Bros., and Colgate), although many other firms contribute to the supply. The larger companies refine not only the crude glycerine which they produce, but also rectify substantial quantities of crude which they produce.

The June issue of "The Fats and Oils Situation", of 1947 shows (28) the supply and disposition of soap in terms of fat content. It also shows the quantity of fats and oils by classes used in the manufacture of soap. The data shown therein may be used to estimate the available yearly output of soap lye crude.

The estimated population in the United States as of July 1,1946 is 143,058,144 people. In 1946 the average civilian soap fat consumption per capita was 12.0 pounds. The average yearly consumption for 15 years was 12.7 pounds per capita. (28). On this basis currently, 1,829 million pounds of soap fats and oils could be expected to be consumed in soaps. The average per capita soap fat consumption for the eight years 1939 - 1946, was 13.6 and 13.9 when including armed services, indicating a total yearly consumption of approximately 2,000 million pounds of fats and oils.

The activity in the synthetic detergent field is bound to have some effect on the consumption of fats and oils in the soap industry. First, because most of the synthetic detergents are derived from petroleum hydrocarbons and secondly, the manufacture of synthetic detergents is one of the fastest growing commercial developments. In 1941, 30 million pounds of synthetic detergent were produced (27) and in 1946, 125 million. In 1948, production is expected to triple that of 1946, while the capacity of 1949-50 is expected to reach over 700 million pounds. Gustav Egloff

(27) predicts the possibility of a billion pounds of synthetic detergents representing 25% of annual soap production within the next few years.

However, it should be pointed out that despite the fact that synthetic detergents are being produced at a rate of about 600 million pounds per year, and that this production is increasing by about 150 million pounds per year every year, the consumption of soap is also rising.

One reason for this is that synthetic detergents are being used for cleaning jobs which were simply left undone in the past, rather than being used as soap substitutes exclusively.

On September 24, 1947, Mr. J. C. A. Faure of Great Britain addressed an audience in Paris and reported the status of the world fats and oils requirements. During war years 1943 and 1944, the United States produced nearly 4.8 million metric tons and in 1946, 4.0 million metric tons. The 1948 production level is expected to be equivalent to 1945 and for the next 3 or 4 years, the United States is likely to become again a net importer, that is, it will take more imports than exports.

Highlights from the International Emergency Food Council (30) disclosed that the total world supply of 1947 was estimated at 10.3 million metric tons, while the pre-war annual average, 1935-1939 was 12.9 million metric tons. This is equivalent to 2.6 million metric tons deficit in 1947. Prospects for the supplies of fats and oils will continue below "effective" demand in 1948, and it is unlikely that the supply will regain pre-war volume before 1950, if then. Meantime, population increases will reach to between approximately 5 to 10 percent above pre-war.

Considering the overall fats and oils situation and the developments in the detergent field, it is estimated here that the average per capita soap, fats and oils consumption will continue at the 1946 level between 1948-1950 of 12.0 pounds, annually. Thus, the outlook for this period is 1,728 million pounds of fats and oils consumed yearly in soaps.

Table VI shows, along with past fats and oils consumed in the soap industry, the theoretically derived soap lye crude production based on present outlooks. The theoretical available saponification crude is also shown.

The 1948-1950 outlook indicates production of 206.5 million pounds of soap lye crude and 34.6 million pounds (395 tank cars) of saponification crude or a total of 244.5 million pounds of crude glycerine annually, 80% glycerol basis. Table IV reveals that such a factory production was only exceeded once in the past - in 1944.

244.5 million pounds of crude glycerine (80% glycerol) is equivalent to 195.6 million pounds of crude on a 100% glycerol basis. On this basis, Table VIII shows that the expected production of crude in the United States for 1948 is 198 million pounds against a consumption of 212 million pounds. This would fall, (Table VI) some place between an average and maximum outlook when considering the saponification crude output. This would be an optimistic outlook for 1948-1950 and could not be depended upon unless glycerine prices continued at a high level and the demand existed.

Table VII shows that the production of crude in U. S. A. since 1920 increased 2.5 fold by 1930; 3.5 fold by 1940, and now approximates five times as much. This production achievement is essentially accounted for by consumer demand increasing the recovery from approximately 50% to a maximum of 88% (92x.95). No further increase in recovery can be economically expected over present-day levels.

TABLE VI

MAXIMUM THEORETICAL SOAP LYE CRUDE PRODUCTION

	(a) Fats & Oils	(f) Theoretical Glycerol Content	Theor. Available Glycerol	(g) Theor. Crude Yields 92% Fat to Crude " 100% Gly.	80% Glyc.	(h) Max. Obtainable Crude 95% Theor. 100% Gly.	80% Glyc.	88%Glyc.
	1000#	%	1000#	1000#	1000#	1000#	1000#	1000#
Avg.1937-41	1,641.989	10.97	180,126	165,716	207,145	157,430	196,788	
1944	1,967,246	10.31	202,823	186,597	233,246	177,267	221,584	
1945	1,749,218	10.22	178,770	164,468	205,585	156,245	195,306	
1946	1,504,886(b)	10.66	160,421	147,587	184,484	140,208	175,260	
Avg.Outlook	1,829,000(c)	10.8	197,532	181,729	227,161	172,643	215,803	
Max.Outlook	2,000,000(d)	10.8	216,000	198,720	248,400	188,784	235,980	
1947-50 "	1,728,000(e)	10.8	189,000	173,880	217,350	165,186	206,483	
			THEORETICAL SAPONIFICATION CRUDE PRODUCTION					
1947-50 Outlook	300,000(i)	10.8	32,400	30,456(j)	38,070(j)	30,456(k)	38,070(k)	34,609(k)
			TOTAL CRUDE OUTPUT					
1947-50 Outlook						195,642	244,533	

(a) Hard oils (tallow class) and quick lathering oils (coco class) used in soap manufacturing. 1937-1946 obtained from "Fats & Oils Situation" (28) Table 8----(b) Low fats and consumption in soap due to limited suppliers----(c) Calculated basis present population at 12.7 pounds per capital yearly consumption---(d)D.V. Stingley of Armour & Co. has reportedly stated (29) that the present total industrial consumption of Fats & Oils and Fatty Acids in the U. S. is now about 3.8 billion pounds:

2000 million pounds - Soap
1000 million pounds - Drying Oils
140 million pounds - Lubricants
650 million pounds - Miscl. Manufactured Products as rubber, leather, plastics, candles, cosmetics, tin, plating,etc..

This figure for soap probably includes fatty acids, the glycerol from which would appear as saponification crude. Nevertheless it is used here as a maximum fat consumption in soaps----(3) It is believed that a yearly per capital consumption of 12 pounds of Fats and Oils in soap will not be exceeded in 1947-50 due to the activity in the synthetic detergent field----(f) Calculated from the classes of fats and oils shown consumed in the Soap Industry(28) Table 8. The glycerol content in the "outlooks" is based on approachment of pre-war level of coco-oil consumption in soaps----(g) A yield of 92% of the theoretical glycerol obtainable from fats and oils to crude may be considered efficient recovery----(h) Not all soapers are in a position to recover glycerine from spent lyes. For many of the small soapers it would be economically unsound to invest in recovery equipment. It is estimated that the maximum recovery of theoretical obtainable crude to market available or usable as raw material for refined glycerine would be 95% of the theoretical---(i)300,000 million pounds of fats and oils (glycerides) are believed by many as a conservative yearly consumption entering the fatty acid field----(j) A 94% yield of theoretical glycerol from the hydrolysis of fats and oils under varying conditions may be considered a fair recovery----(k) Most of this crude may be considered available since most manufacturers engaged in fat splitting find it economical to concentrate their sweet water to 88% saponification crude. 100% recovery is closely approached.

TABLE VII

CRUDE GLYCERINE IN U. S. A.

Basic 100% Glycerine
In 1000 Pounds

(a) Year	(a) Opening Inventory	(a) Production	(a) Imports	(a) Exports	(a) Closing Inventory	(a) Calculated Consumption	(a) Reported Consumption
1920	11,240	43,750	—	---	18,260	---	---
1921	18,260	51,160	—	---	21,330	---	---
1922	21,330	68,270	—	---	20,710	---	---
1923	20,710	79,660	—	---	20,760	---	---
1924	20,760	76,120	--	---	21,040	---	---
1925	21,040	82,730	--	---	12,370	---	---
1926	12,370	93,100	—	---	20,970	---	---
1927	20,970	102,570	--	---	36,520	---	---
1928	36,520	104,400	—	---	31,650	---	---
1929	31,650	112,060	—	---	26,660	---	---
1930	26,660	110,940	--	---	25,880	---	---
1931	25,880	112,000	10,138	328	34,430	113,255	---
1932	34,430	107,140	5,382	260	44,500	102,192	---
1933	44,500	95,850	3,473	---	24,200	---	---
1934	24,200	122,500	15,081	---	32,980	---	---
1935	32,980	112,948	8,221	3,353	34,400	116,396	---
1936	34,400	123,277	11,149	1,146	31,180	136,500	---
1937	31,180	135,231	13,441	1,375	56,080	122,397	---
1938	56,080	129,696	13,097	3,746	77,670	117,463	---
1939	77,670	147,581	10,988	7,399	70,890	157,950	---
1940	70,890	157,856	9,096	12,464	72,120	153,268	---
1941	72,120	195,283	9,020	9,585	60,349	206,489	207,871
1942	60,349	177,435	6,105	32,638	56,659	154,592	189,034
1943	56,659	171,933	9,821	24,563	30,914	132,936	169,902
1944	80,914	199,834	5,859	9,111	67,681	189,815	204,915
1945	87,681	172,450	9,318	7,598	45,710	216,241	180,717
1946	45,710	156,823	9,809	654	43,154	168,539	162,322
1947	43,154	207,768	2,840	4,268	48,582	200,912	209,110
1948 (est.)	49,000	198,000	---	---	45,000	202,000	212,000

(a) Data collected from Facts for Industry, Fats & Oils, Bureau of Census, Dep't. of Commerce, 1941-1945, 1942-1947, and 9 months in 1948; also from "Glycerin", Industrial Reference Service, Bureau of Foreign and Domestic Commerce U. S. Dep't. of Commerce----
(b) See Table VIII.

TABLE VIII

1948 CRUDE PRODUCTION IN U. S. A. (a)
Basis 100% Glycerine in 1000 Pounds

	Production	Consumption
January	20,403	21,781
February	18,413	19,696
March	19,522	20,389
April	15,578	16,049
May	15,482	15,077
June	16,915	19,438
July	9,519	11,137
August	15,999	17,186
September	15,582	17,586
TOTAL - 9 months	147,413	158,339
TOTAL - 1948 (est.)	198,000	212,000

(a) Data collected from Facts for Industry, Fats and Oils Unit Bureau of Census, Department of Commerce

TABLE IX

REFINED GLYCERINE PRODUCTION IN U. S. A. (a)
Basis 100% Glycerine in
1000 Pounds

		Dyn., H. G., Y. D.	C.P.	Total
1940		70,837	85,085	155,922
1941		86,215	108,112	194,327
1942		107,523	73,058	180,581
1943		96,467	63,242	159,709
1944		96,865	99,205	196,070
1945		89,530	83,284	172,814
1946		64,180	84,383	148,563
1947		91,388	99,765	191,153
1948	January	8,701	10,437	
	February	7,947	10,294	
	March	7,699	11,350	
	April	6,715	8,293	
	May	6,383	7,704	
	June	8,772	9,050	
	July	4,573	5,838	
	August	7,045	8,991	
	September	6,886	9,484	
TOTAL - 9 months		64,721	82,441	
TOTAL, 1948 (est)		87,000	110,000	197,000

(a) Figures from Facts for Industry, Fats & Oils, Bureau of Census, Dep't. of Commerce ------

In terms of refined glycerine, 244.5 million pounds of crude glycerine (80% glycerine), considering a yield of 97%, and an average market grade of 97.5% glycerol, is equivalent to 194.6 million pounds. The estimated consumption of refined glycerine in the United States, 1948-1950, will be 192 million pounds annually. (Table I). It should be mentioned that no allowance has been made so far for net exports which affects total disappearance.

Table IX shows that an expected production of refined glycerine in the United States for 1947 was 190 millions. This is just below the overall estimated demand.

The demand has reached the possible present-day level of supply from natural sources.

SYNTHETIC GLYCERINE PRODUCTION: During the first World War and as late as 1940, the chemical world had avoided or had but little success with synthetic glycerine. Production of substitutes was resorted to rather than attempting to make synthetic glycerine at a price comparable with the natural product, by-product of the soap-making industry.

The Shell Chemical Corporation in August, 1948 started the commercial manufacture of synthetic glycerine from propylene in an $8 million plant located at Houston, Texas. The annual plant capacity is 30-35 million pounds (27). It is believed that as much as 20-22 million pounds of this synthetic glycerine have been contracted for annually for the next few years.

In 1936 a survey by the Shell Development Co. disclosed that new and increased uses of glycerine were bringing the supply and demand sufficiently close together to justify a shortage of glycerine in the near future. This apparent outlook, together with wide fluctuations in glycerine price and the unsuccessful attempts to make a high grade glycerine at economical cost by fermentation processes led to the belief that synthetic glycerine had considerable possibilities.

SHELL'S SYNTHETIC GLYCERINE PROCESS: Of the numerous syntheses possible for glycerine Shell(31) felt that the most direct are those starting with the three carbon skeleton. Their attention was directed to the unlimited amounts of propylene and propane that were available.

Thousands of investigations suggested a synthesis starting with propylene to allyl chloride to allyl alcohol, or to glycerine dichlorohydrin to glycerine. The discovery of the "hot chlorination" of propylene made the process feasible.

Actually two alternate possible methods exist for the conversion of allyl chloride to glycerine. Allyl chloride is formed by a combination of 3 to 5 mols of preheated propylene (400°C.) with a mol of chlorine. The resultant reaction occurs at 500-530°C., and the allyl chloride which is formed in yields of 80% or better can be purified by fractional distillation.

Allyl chloride can be treated in two ways: (1) hydrolysis to allyl alcohol, chlorhydrination to monochlorhydrin and hydrolysis or (2) direct chlorhydrination to glycerine dichlorohydrin and hydrolysis.

The fact that Shell has announced the production of several million pounds of by-product trichloropropane yearly indicates that the second method has been chosen.

The dilute saline glycerine solution, after concentration in multiple-effect evaporators, must be desalted, and vacuum distilled to a 99% purity.

When this plant is working at capacity production, it has been estimated that glycerine can be sold profitably at about 25¢ per pound.

At first, considerable difficulty was encountered in purifying the prepared glycerine to meet U.S.P. standards. A very successful method was finally established.

The original synthetic glycerol is obtained in a dilute crude form. This is concentrated in much the same way as spent soap lyes. By making appropriate cuts during the distillation, extracting with a solvent as xylene (U.S. Patent 2154930)*and redistilling, a glycerine is secured which meets all commercial specifications.

The ultimate overall yield of finished glycerine from allyl alcohol is approximately 90 per cent.

TYPICAL ASSAY OF SHELL'S SYNTHETIC GLYCERINE AND ITS TOXICITY: A claim is made that this synthetic glycerine will be better than any glycerine offered in the market:

The following was given as a typical assay:

Density 20/4	- 1.2611
Chlorine	- 0.002 %
Acids and Esters	- 0.002 (6) equiv. per 100 grams
Readily Carbonizable Substances	- Straw color - passes U. S. P.
Taste	- Sweet
Odor	- Not detectable
Color (Pt-Co)	- 0.5-practically 0.

Mr. E. Ross Hart, as disclosed in a publication (33) of the University of California, made a "Pharmacological Comparison between Synthetic Glycerol and Glycerol prepared from Natural Oils."

. . . .

* A copy of this patent may be found at the end of this report.

This research was supported by the Shell Development Co. and the glycerine put to test was made synthetically from the toxic intermediates, allyl chloride and allyl alcohol. It was revealed that chemically undetectable amounts of these contaminants may occur in the final product and that this synthetic glycerine from propylene presents possibilities of use in foods, beverages, and pharmaceuticals. It was not possible to demonstrate any significant difference between pharmacological properties of the sample of glycerine prepared from propylene and those of glycerol derived from natural fats and oils. The conclusion, therein, was as follows: -

"Investigations of toxicity on oral administration, local irritation, and effect on striated muscle have shown no significant differences between synthetic glycerol and the product obtained from natural fats and oils." This would mean that synthetic glycerine can be used as a plasticizer for cellophane.

INTERMEDIATES AND DERIVATIVES FROM SHELL SYNTHETIC GLYCERINE PROCESS:

A number of intermediates and derivatives will be made commercially available by the Shell synthetic glycerine process. Formerly, these were made in quantity only by synthesis from glycerine. The developments of such compounds in the past were hampered by the uncertainty of glycerol prices. It is believed that on the development of outlets for these intermediates and derivatives rests an economically successful process of glycerine which would be reasonably competitive to the natural glycerine products from fats and oils. The promotional efforts being made by Shell substantiate this opinion as to their objective.

H. GLYCERINE REFINERS: PLANT LOCATIONS: Table X represents the compiled data that was collected on manufactures of refined glycerine.

TABLE X

MANUFACTURERS OF REFINED GLYCERINE IN THE U. S. A.

Company	Plant
Proctor & Gamble Co.	Long Beach, California Staten Island, N. Y. Dallas, Texas Baltimore, Maryland Quincy, Massachusetts St. Louis, Missouri Chicago, Illinois Cincinnati, Ohio
Colgate-Palmolive-Peet Co.	Berkley, California Jersey City, N. J. Brooklyn, New York Jeffersonville, Indiana Kansas City, Kansas
Lever Brothers Co.	St. Louis, Missouri Hammond, Indiana Baltimore, Maryland Cambridge, Mass.
Shell Chemical Corp.	Houston, Texas
Armour and Co.	Babbitt, N. J. Chicago, Illinois
Swift and Co.	Chicago, Illinois
Harshaw Chemical Co.	Philadelphia, Pa. Cleveland, Ohio
Reichhold Chemicals, Inc.	Detroit, Michigan
Pacific Soap Co.	San Diego, California
E. F. Drew Co.	Boonton, N. J.
Beach Soap Co.	Lawrence, Mass.

Source - Chemical Engineering, Oct. 1948, p. 335.

From Table X, it may be seen that there are now 10 glycerine refiners of the natural product from fats and oils with twenty-six plants and one manufacturer of synthetic glycerol from propylene in the United States. The overall production level of market refined glycerine will be in the neighborhood of 217 million pounds yearly starting with 1948.

There are many users of glycerine but the end consumer of glycerine in products etc. is the public. Glycerine is sold to processors of various products closely located to their key market locations. It follows, therefore, that the principle market for glycerine will be close to highly populated areas.

I. GLYCERINE PRICES: TRENDS: OUTLOOK: Economically speaking, since the turn of the century, glycerine has been in a bad way. The price of this important commodity has always been affected by the fact that glycerine production was not controlled, chiefly due to its being a by-product of the soap industry.

Furthermore, the price of glycerine has never actually borne any definite relation to the price of soap-making raw materials. Soap production varies directly in effecting soap lye crude glycerine output, but the average efficiency of recovery only improved as consumer demand increased the urge for production. Today, primarily on account of the demand for glycerine with essentially the same existing plants, glycerine recovery has reached an economical high overall yield of approximately 88% from consumed soap fats to crude. From 1928 to 1939 inclusive, the average efficiency of recovery of glycerine advanced from 50 to 75 percent.

The fatty acid industry also supplies recovered glycerine in the form of saponification crude. Previously less, but presently it accounts for 16 per cent of the total available crude. The recovery yield in this industry is as high as 94 per cent.

The law of supply and demand alone has dictated the prices of refined glycerine. However, the present-day demand has reached the possible supply of glycerine in the form of by-product of the soap and fatty acid industry.

In examining the trend of prices in the past (40), the price of C.P. glycerine rose from 11¢(1906) to 20¢(1910). The high and low for 1910-1915 were 26¢ and 16¢ respectively.

At the outbreak of hostilities in 1914, World War I, the countries of Europe were found with very limited stocks of glycerine. As a point of interest, the estimated world production of glycerine in 1913 was 135 million pounds per annum, with the United States producing 40 million pounds of this total, calculated on the basis of the 80 per cent crude. On account of war demands the price of C. P. glycerine went from 22¢ in 1915 to 60¢ on the first of 1916. During 1916 there were some fluctuations, the high was 60¢, and the low 37¢. In 1917 the price of C.P. glycerine rose from 52¢ to 67¢ with a high of 70¢. With a sudden decrease of glycerine demand, toward the end of 1918 the price dropped sharply from 67¢ to 16.5¢. During 1919, the price went to 24.5¢.

Figure 2 reveals the trend of C.P. glycerine from 1920 to date. It also shows the price of soap lye crude since 1938. The price of saponification crude is usually 1¢ higher than soap lye crude when the price is approximately 8¢. In the range of 20¢ and 30¢ for soap lye crude, the price for saponification crude is normally 2¢ and 3¢ higher, respectively, etc.

In contrast to the condition that existed prior to the first war, the production of crude in the United States by 1939 had risen to 184.5 million pounds and the world output was probably 350 million pounds. During these twenty-five years the situation had changed considerably. The consumption of glycerine had increased tremendously and the warring countries of Europe were in an excellent position as far as glycerine was concerned. All during World War II hostilities, the price of C.P. glycerine was reasonable, if not low, due to control by the Government.

On January 1, 1944, glycerine was removed from specific allocation, allowing most civilian glycerine users the quantity used in 1940. Prior to 1944, some civilian users were seriously curtailed. By May 13, 1944 the War Food Order 34 was revoked. With the expiration of O.P.A. ceilings temporarily on about July 15,1946, the price of C.P. glycerine immediately shot up to as high as one dollar per pound in some transactions. The average selling price was probably 55½¢ per pound. However, the OPA ceilings were restored on approximately August 1, 1946. On about November 14, 1946, the OPA ceiling price for C.P. glycerine was removed and Figure 2 shows the story. The price rose to 76¢ and by January 1947 began tapering off reaching 29½¢ by July 1947. Since November 1947 the prices for C. P. glycerine have been on an incline.

Most refiners resented the condition that existed prior to the end of OPA ceilings. There was a ceiling selling price on domestic refined glycerine, but on account of the demand, imported glycerine which was removed from such ceilings, sold for as high as 91¢ per pound.

It is apparent from the current trend of prices that future increases in glycerine consumption will largely depend upon a reasonable and steady price level. It may be noted in comparing prices of Figure 2 and corresponding disappearance figures of Table IV, that the consumption of glycerine increased when the price was steady and reasonable.

The announced production of synthetic glycerine changes the enjoyed situation of supply and created demand for the glycerol refiners from fats and oils. Unless maximum recovery yields are maintained to assure reasonable price stability to the consumer, additional synthetic glycerine plants may enter the picture eventually, affecting their by-product outlet. Of course, this is on the assumption that glycerine consumption remains within the controllable limits of soap manufacturers. In the long run, fermentation glycerine and large imports of it may be possible.

If the glycerine consumption increases and records indicate that it has not levelled off for any length of time, the price stability that will no doubt result by the availability of synthetic glycerine should be welcomed by users, providing the natural refiners can produce glycerine comparable in quality to the synthetic glycerol. Since the soap and fatty acids industry has reached the peak of its output of glycerine, basis fat and oil consumption, the synthetic glycerine also puts a check on the infiltration of glycerine substitutes primarily due to high prices.

J. TARIFF: Agreements reached by negotiation with twenty-two nations at the Geneva Conference concerning tariff cuts under international agreement have been made public by the United Nations (41). Crude and refined glycerine were among the selected list of goods imported into the United States for which tariff concessions were made. The agreements on glycerine effective January 1, 1948, are as follows: -

	Existing rate cents per lb.	Proposed rate cents per lb.
Glycerine, Crude	0.8	0.4
Glycerine, Refined	1-7/15	I

Whether there will be any separate trade agreements with duties below the proposed rate, as in the 1945 tariff rate (42), is still to be determined. The low tariffs may indicate the possibility of making glycerine in molasses rich countries and shipping it to the United States for consumption.

K. IMPORTS AND EXPORTS: Table IV shows the total imports, exports, and net imports or net exports since 1919. From 1920 to 1938 the United States imported a net average of 15 million pounds of crude and refined glycerine yearly, basis 80% glycerol. The bulk of these imports was in the form of crude glycerine.

In 1939, the net imports were only 2.6 million pounds. Then from 1940 to 1945 inclusive, net averages of 11.5 million pounds were exported.

In 1946, 24.3 million pounds, 80% glycerol basis, were the net import. Approximately sixty percent of this import was refined glycerine, a record high for refined glycerine imports into this country. This may be attributed to the fact that U.S. factory production was below the existing demand, chiefly on account of the producers' and refiners' outlook on existing market conditions. Nevertheless, the total consumption was not far below normal; but aside from the large imports of refined glycerine, the stock on hand the first of 1946 was reduced almost 50% by the end of the year.

In 1947, the production was some 60 million pounds over that of 1946, and a 12 million pound increase is estimated for the 1948-50 outlook (see Table VI.) With such a production, the demand will be met.

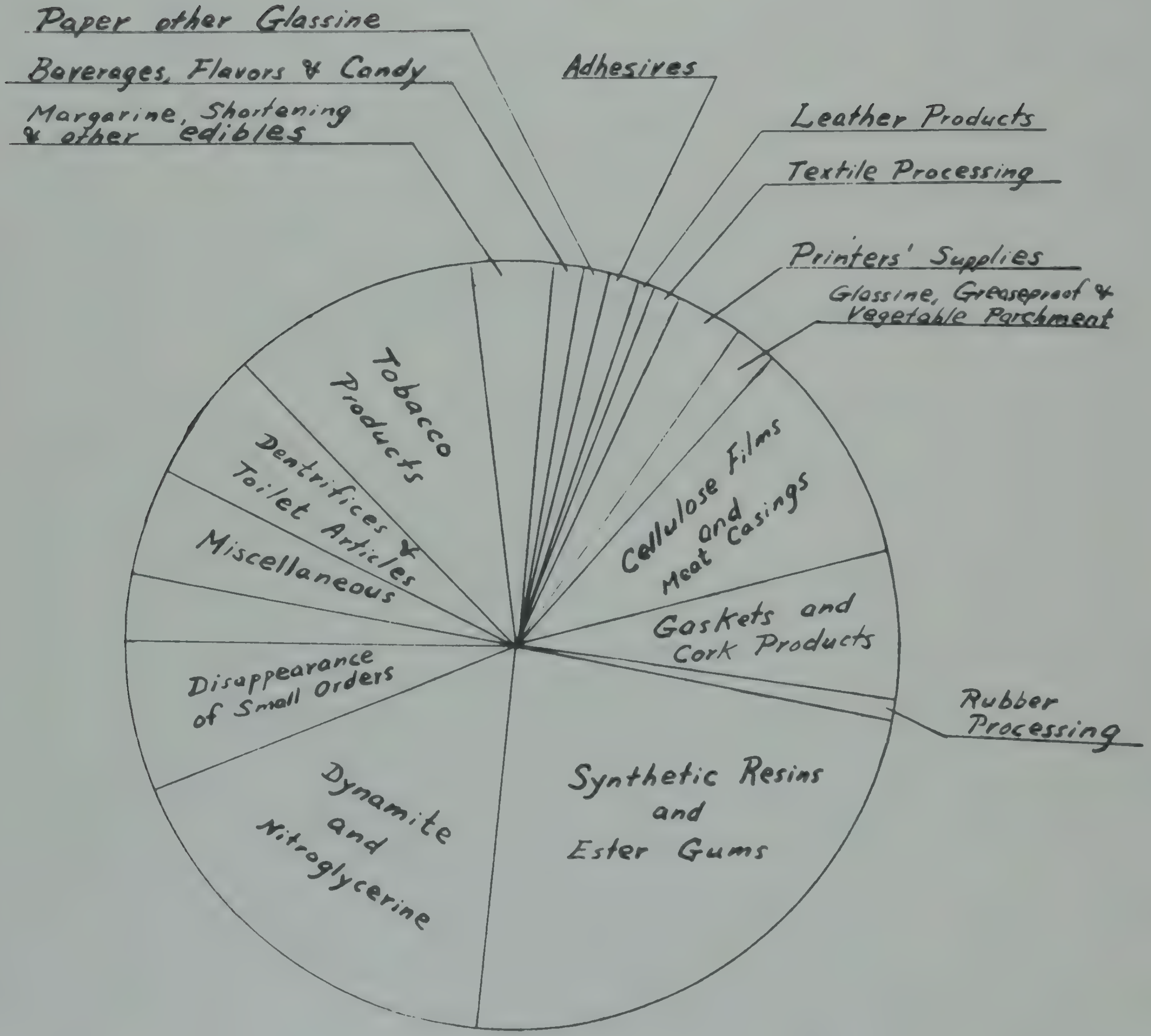
During 1947, the net exports were 1.5 million pounds. This substantiates the general consensus that the United States will become an exporter in the immediate postwar years. Two to three million pounds of glycerine may be exported yearly (14).

Prior to the war, Canada was the largest foreign market but with an increase in her output other markets must be counted on. Past records of exports are of little significance, primarily because of fat and oil shortages abroad which are expected to continue until 1956. European and Asiatic countries present themselves as especially good markets. U. S. S. R. could occupy first place as an outlet for our refined glycerine, depending upon trading relationships. Mexico, Cuba and South American countries could be developed to larger markets than they are today.

Except in 1946, crude glycerine imports have been much larger than the refined grade. Argentina and Cuba have been the main suppliers since World War II. Besides these countries, U.S.S.R. and the Philippines were fair sources prior to the war. In 1943, Canada and Uruguay accounted for one third of the total import.

The yearly outlook for total disappearance of market grade refined glycerine in the United States during 1948-1950 may be estimated as from 195 to 202 million pounds. This considers a yearly consumption of 192 million pounds in this country and a net export of from 3 to 10 million pounds yearly. Until synthetic glycerine production goes into full swing, net exports probably will not exceed two million pounds per annum. Molasses glycerin may well enter the picture in the forseeable future. The Glycerine Corporation of Cuba, which is a U. S. owned company, is building a glycerine plant in Matanzas which will be based on molasses (43).

Estimated Consumption of Glycerine
Classes of Products in the U.S.A. 1948-50



Weight Percentage Breakdown
of
1948-1950 yearly average consumption:
192 million pounds

R. S. ARIES & ASSOCIATES

Source: Table I.

Figure 1

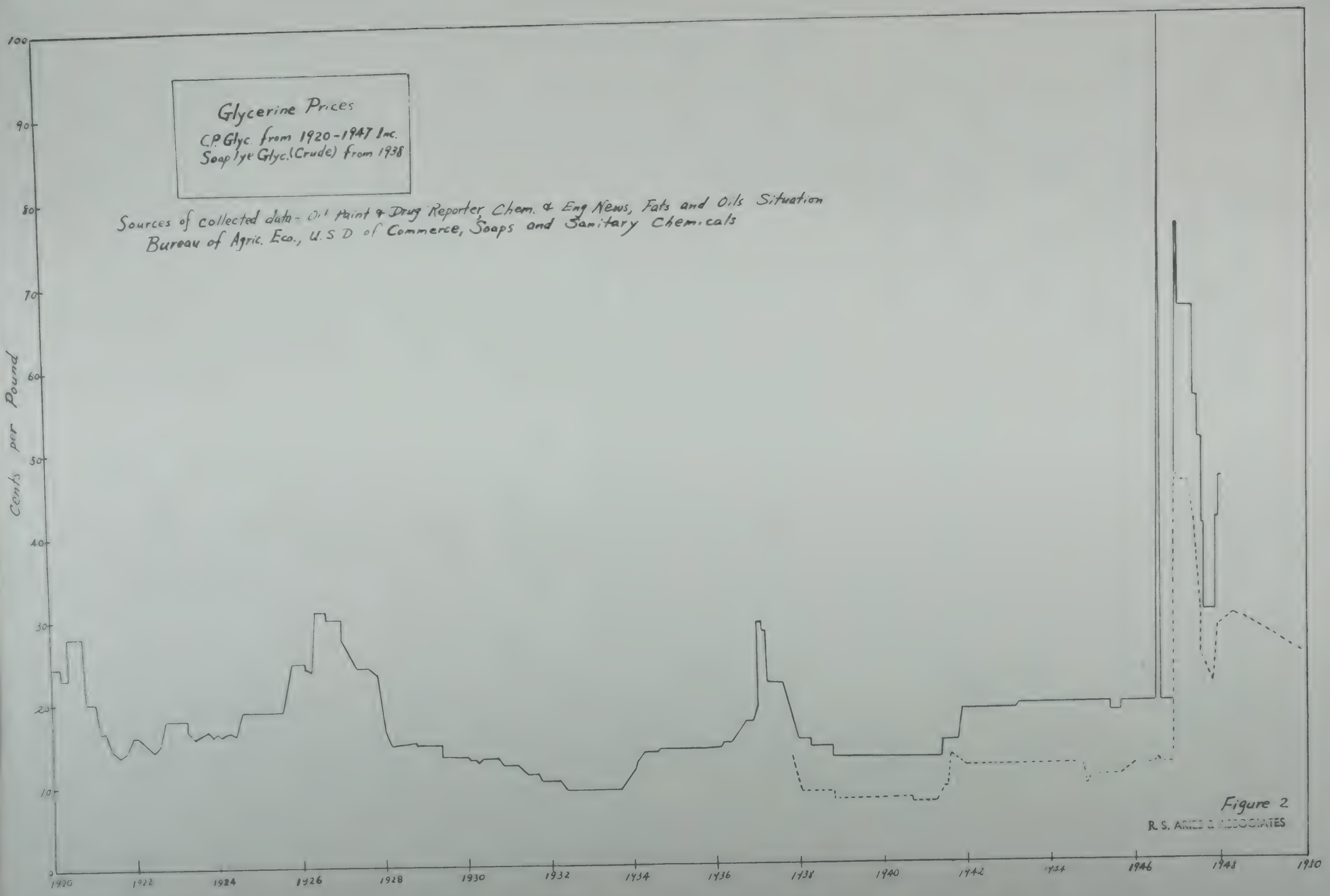


Figure 2

R. S. ARIES & ASSOCIATES

V. THE PRODUCTION OF GLYCEROL FROM SUGAR BY FERMENTATION.

Digest of the Final Report on S.R.F. Project No. 5
by Carl Neuberg, New York University.

The production of glycerol from sugar by fermentation with yeast is a problem which was developed during the last world war. The methods in use are based on the recognition that acetaldehyde is formed as an intermediate in the breakdown of sugars in alcoholic fermentation, and that its immediate precursor pyruvic acid, by decarboxylation under the influence of carboxylase, is responsible for the terminal carbon dioxide of the fermentation.

In an equilibrated system, as is actually the alcoholic cleavage of sugar, a trapping of the aldehyde step or elimination of acetaldehyde by other means than its final reduction to ethanol, demands the equivalent accumulation of another reduction product. To bring about this condition, reactants had to be found which only attacked the acetaldehyde step without impeding the enzymatic decomposition of sugar. This result can be achieved in two principally different ways. The one is qualified as purely chemical, the other one as biochemical.

The purely chemical way consists of trapping the acetaldehyde either by binding or condensation. Suitable agents for this purpose were on one hand the sulfites, on the other hand dimedon (dimethyldihydroresorcinol), and certain hydrazine derivatives reacting with sugar very slowly, as for example, semi-carbazide, thiosemi-carbazide, or 2,4-dinitrophenylhydrazine (in neutral medium).

The second principle is the protection of acetaldehyde from its normal course of reduction to the final product ethanol, the so-called biochemical dismutation. The latter causes a biochemical Cannizzaro reaction, i. e., the dismutation of two molecules of acetaldehyde to one molecule of acetic acid and one molecule of ethanol. This enzyme reaction takes place when the mutase (oxydo-reduction) system is activated by hydroxyl ions.

The elimination of acetaldehyde by carboligatic reaction demonstrates another biological principle. In the latter case acetaldehyde is being combined with another aldehyde added to the mash, as for example with acetaldehyde under the formation of acetoin (acetylmethylcarbinol).

Both types elucidate clearly the removal of acetaldehyde, i.e., of an oxidative step. It could not be predicted that the yeast would then perform its correlative reduction work by accumulating an equivalent amount of glycerol.

These theoretical foundations were built by Neuberg and co-workers in the years 1916-1921.

For economic reasons only two methods for biochemical glycerol production are practicable.

1. The fixation of acetaldehyde employing sulfites and
2. The elimination of acetaldehyde by dismutation using weak alkalis, as for example, sodium carbonate, magnesium hydroxide, or alkali phosphates.

Both methods have been employed technically. The sulfite process was protected for Connstein and Luedecke under the German Patents 298,594; 298,595; 298,596, May 1916, and U.S.P. 1,368,023*, Feb. 8, 1921; 1,511,754,* Oct. 14,1924; whereas the alkali carbonate process was protected by Eoff under U.S.P. 1,288,398*, Dec. 17,1918.

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* A copy of this patent may be found at the end of this report.

The yields of glycerol on sugar obtainable in sulfite fermentations have been determined by Neuberg and co-workers (Neuberg and Reinfurth, Ber. 52, 1677, 1919), as follows:

33g	Na_2SO_3	on 100g	sugar	11.90g	CH_3CHO	23.37g	$CH_2OH.CHOH.CH_2OH$
50	"	" 100	"	12.52	"	24.86	"
75	"	" 100	"	13.89	"	27.61	"
150	"	" 100	"	18.65	"	36.90	"

The equation

$$C_6H_{12}O_6 = CH_3CHO + CO_2 + C_3H_8O_3,$$

or if the participation of sulfite is considered,

$$C_6H_{12}O_6 + Na_2SO_3 + H_2O = C_3H_8O_3 + CH_3CH(OH)OSO_2Na + NaHCO_3$$

is valid at every moment of the fermentation for all sulfite concentrations. The maximal yield of glycerol for 180 g sugar could be 92 g glycerol or 51 per cent. In practice only about 72.6 per cent of the theoretical yields were achieved. This fact is caused on one hand by the yeast not being able to endure larger sulfite concentrations, — and on the other hand by that part of the sugar which is not incorporated in the above equation and decomposes by normal alcoholic fermentation to ethanol and carbon dioxide. The yield of 39.18 percent of glycerol on sugar was achieved only with a special strain of yeast, saccharomyces Saké, which is especially insensitive against large salt concentrations (Kumagawa, Bio. Z. 131, 148, 1922). According to Connstein and Luedecke,(Ber. 52,1385, 1919) only 34.6 per cent glycerol yield was obtained by analysis with a simultaneous yield of 17.6 per cent acetaldehyde. The above workers found either too much or too little aldehyde; they did not recognize its formation equivalent to glycerol.

The low yield of glycerol isolated in practice, 19 - 21 g of glycerol per 160 g sugar, is only caused by the great difficulties of the purification of fermentation glycerol.

In the dismutation process glycerol yields of 14.2 per cent were achieved according to the statements of Neuberg, Hirsch, and Reinfurth (Bio. Z. 105, 307, 1920).

The extraction of the acetic acid formed simultaneously was tried by J.W. Lawrie, U.S.P. 1,909,183; May 1933, but would hardly pay; whereas it is profitable to isolate the acetaldehyde formed in the sulfite fermentation method. During the purification of the glycerol the acetaldehyde is automatically set free from its bisulfite compound. Alkali carbonate formed from bicarbonate in the concentration of the glycerol mash sets the acetaldehyde free from its bisulfite compound according to the following equation:-

$$CH_3CH(OH)OSO_2Na + Na_2CO_3 = CH_3CHO + Na_2SO_3 + NaHCO_3$$

The equivalent formation of acetic acid, ethanol, and glycerol in the so-called third form of fermentation (Neuberg and Hirsch, Bio.Z. 100, 316, 1919)

$$2\ C_6H_{12}O_6 + H_2O = C_2H_5OH + CH_3COOH + 2\ CO_2 + 2\ C_3H_8O_3$$

was not recognized by Eoff, Lindner, and Beyer (Ind. and Eng. Chem. XI, 842, 1919)

Insignificant modifications have been described, but as far as known, have not been used in practice. One of those modifications for example was the addition of "catalysts" to the sulfite fermentation which allegedly increased the glycerol yield. It cannot be clearly seen, nor has it been proven, that the suggested addition of iron, cobalt, nickel, manganese salts, and the like actually improved the glycerol yield. It is also not understandable why these oxidation catalysts should improve the yield of a material formed by biochemical reduction. The respective patent owners probably gave those specifications in order to try to make some profit even after the original sulfite patents had expired.

In a patent application by Hugo Haehn (German application; Oct. 31, and Nov. 28, 1936; French Patent 829,263, June 17, 1938; British Patent 488,464, July 7, 1938; and U.S. P. 2,189,793*, Feb.13, 1940), the inventor transmits to the sulfite process, without especially mentioning it, the well-tried method of producing yeast by aeration. He wants to cut the longer lasting fermentation time by injecting air for about 8-10 hours. He furthermore claims to have achieved an increase in glycerol yield up to 34 per cent.

It was an important task to examine these claims, because a diminution of the fermentation time, as well as an increase in glycerol yield constitute economically important factors.

A thorough study of glycerol fermentation in the presence of sodium sulfite, with simultaneous injection of oxygen, has been undertaken by Dr. Neuberg together with Mrs. Gertrude D. Maengwyn-Davies.

The experiments were set up in the laboratory in the following manner. Series of sulfite fermentations under practically anaerobic conditions were run, simultaneously fermentations with the injection of oxygen from a gas bomb, air, nitrogen, or carbon dioxide were set up. The experimental conditions were varied by fermenting partly at room temperature (18° - 24°C), partly in an incubator at 30°, and 36°C.

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* A copy of this patent may be found at the end of this report.

The experimenters were unable to achieve Haehn's fermentation time of 8-10 hours, but it has to be considered that Haehn used a special apparatus for fine aeration. This procedure is different from the one used since the laboratory was only equipped for simple gas injection.

A possibility existed that the diminished fermentation time was simply caused by the better distribution of the yeast, i.e., by the swirling of the mash owing to the injection of oxygen or air. Therefore, further experiments were undertaken employing other gases, namely, nitrogen and carbon dioxide, always simultaneously with fermentations without using any gas.

A few words should be said regarding the analytical methods employed. The determination of acetaldehyde was undertaken after Neuberg and Reinfurth (Bio.Z.89, 365,1918), Kobel and Neuberg (Handbuch der Pflanzenanalyse IV,1264-66,1933), as well as Neuberg and Gottschalk (Bio. Z.146, 164,1924), with three practical significant modifications. The determination can be undertaken either in the clear centrifuged mash, or after the simple purification of the mash with barium chloride (precipitation of the excess sulfite and the sulfate formed). Instead of the formerly used p-nitrophenyl-hydrazine acetate, 2,4-dinitrophenylhydrazine hydrochloride was employed.

The value found for acetaldehyde is exact when the determination is carried out in the following manner. The 2,4-dinitrophenylhydrazine hydrochloride is dissolved in 2 N hydrochloric acid, to this solution an absolutely clear aliquot of the mash is added at room temperature, and left standing for about 12 hours. The acetaldehyde originally present in its bisulfite complex is thus precipitated without any loss. Only after this incubation period in the cold, is the determination mixture heated on the water bath for 1 to 2 hours. During this period free reagent goes into solution, and the acetaldehyde-2,4-dinitrophenylhydrazone precipitates in a well filterable form. It is advisable to add 2 N hydrochloric acid during this heating period. The material is then suctioned off hot through a glass sintered gooch crucible, first washed with cold 1 N hydrochloric acid, and then with cold distilled water. The crucible is dried in vacuo to constant weight.

The acetaldehyde determination can also be undertaken by distillation over calcium carbonate with especially good cooling. The mash is prepurified with barium chloride. This procedure gives good results but the possibility of loss is obviously increased.

Glycerol determinations were made after the following purification procedure: The excess sulfite and sulfate was precipitated boiling hot with barium- or lead acetate after Neuberg and Reinfurth (Bio. Z. 89, 363, 1918). The same method is later also employed by Tomada (J. Soc. Chem. Ind., Japan, 48, 76, T, 1929), and known in this country as the Tomada method. The excess barium or lead is precipitated hot with sodium carbonate. The filtrate is acidified with acetic acid and concentrated on the water bath. The separation of glycerol from the salts and other materials can be done with alcohol-ether as usual. It is unnecessary to use this further purification when the material is made up to volume after the soda treatment, acidification, and concentration, as ethanol and acetaldehyde escape. The glycerol is then determined after the Zeisel-Fanto, Stritar method in an aliquot part. The last traces of alcohol escape definitely when the material is further concentrated in the Zeisel apparatus as prescribed for the determination. Correct values can only be obtained by the Zeisel-Fanto method, whereas with the periodate (Malaprade: Soc. Chim, France, Bull. 43, 683,1928; modification by Fleury and Fatome: J. de Pharm. et Chim. ser. 8, 21,247, 1935) and cerate (Fulmer, Hickey, and Underkofler, Ind. Eng. Chem. Anal. Ed. 12, 729,1940) methods the glycerol amounts found are too high.

These methods, excellent per se, fail for fermentation glycerol because the agents employed therein tend to oxidize other materials present in mashes which do not yield alkyl iodide in the Zeisel-Fanto method.

It must also be taken into account that during aeration the sulfite used as trapping agent might be either directly oxidized to sulfate, or that a halving partition of the oxygen action between sulfite and substrate might be manifested. The latter is a consideration coming to mind when one compares conditions to those found by Neuberg and Kobel for glyoxal or methyl-glyoxal in the presence of sulfite, where the former are oxidized to glyoxylic or pyruvic acid and the latter to sulfate. Sulfite-sulfate balances were therefore carried out. The experiments showed that comparatively little sulfite was oxidized to sulfate even on oxygen injection. The oxidation balance amounted to 13 per cent if the determinations were carried out at the exact time when all the sugar had been fermented. When oxygen is being injected for a longer and unnecessary period, i.e., after termination of the biological process, oxidation up to double the above percentage can be obtained. When air was employed the oxidation reached 4 per cent only. an amount by no means larger than the absolutely unspecific oxidation taking place without any gas injection.

When nitrogen was injected the oxidation balance had practically the same percentage value. The sulfite-sulfate balance was determined after Neuberg and Reinfurth.

When injecting nitrogen the glycerol yield was the same as on aeration, but the fermentation time increased from 14-18 hours to 98 hours.

For comparative purposes, since gas injection causes similar phenomena as stirring, fermentations with stirring and without gas injection were set up. The fermentation time was also considerably cut, namely to 24 hours. In this case the mash was not stirred with exclusion of air so that air might have been stirred in, despite the carbon dioxide atmosphere produced by the fermentation.

The equation for the second form of fermentation

$$C_6H_{12}O_6 = CH_3CHO - CO_2 + CH_2OHCHOHCH_2OH$$

is no longer valid when working with gas injection. The gas stream frees acetaldehyde by dissociation from its bisulfite complex, which was verified as follows: The gas after it left the mash passed through wash bottles containing sodium bisulfite or hydroxylamine solution. The acetaldehyde, easily traceable by the sodium nitroprusside reaction, was found in its bisulfite complex or as acetaldoxime.

Carbon dioxide injection showed a bad effect on both top yeast brands employed (Fleischmann and National Grain, both baker's yeast). The sugar was not fully fermented even after 6 days and the yeast had died. Fresh yeast added during this period had died also.

The yeast was still alive, although in different conditions, at the end of the fermentation experiments when oxygen, air, or nitrogen were injected, as well as when no gas at all was employed.

These results allow us to draw the following conclusions: The beneficial action of the aeration (diminution of fermentation time) is caused by the improved state of the yeast under the detrimental conditions of the sulfite substrate. A stimulation by oxygen cannot be the sole cause, as the yeast shows practically the same behavior when nitrogen is used, except for the lengthened fermentation time and a slightly worse physiological state. Yeast growth on nutrients cannot be fully excluded. The amount of nitrogen added is 0.064 g.nitrogen, i.e., maximal equivalent to 0.4 g protein for 6 g of yeast (dry substance 1.8 g). The protein might amount tb approximately 0.8 g yeast. In fact, experiments without nutrients showed that the glycerol yield was identical, but the fermentation time increased to about triple. It was still considerably shortened in comparison to a fermentation run without any gas with and without nutrients. The nutrients demonstrate a combined ionic influence. Whereas the fermentation time was cut to 14-18 hours when a mixture of the nutrients was employed, it was increased to 46-50 hours with only magnesium sulfate, and even to 72 hours with ammonium phosphate alone. When not using any gas the fermentation time is the same with and without any nutrients, namely 140 hours.

It was dogma up to now that sulfite fermentations could only be undertaken with top yeast. In the present work it has been established for the first time that sugar can be fermented for glycerol using brewer's yeast. We employed yeast from the Piel Brewery. When the amount of bottom yeast used is about triple the amount of top yeast, the fermentation time is nearly doubled. The glycerol yield is lower when too large amounts of yeast are employed but remains considerable. Unexpectedly fermentations without any gas were finished within 50 hours.

The preliminary results of the present work can be seen from the enclosed table.

TABLE:

All set ups had the same composition as follows:

A	15 g glucose 9.3 ammonium phosphate $(NH_4)_2HPO_4$ 90 ml tap water
B	9 g disodium sulfite 0.15 magnesium sulfate 60 ml tap water

Half the amount of yeast was added to solution A until the mash fermented visibly, then solution B dripped in during an average time of 2 hours. After another 30 minutes standing the second half of the yeast was added. After yeast addition the mash was always shaken thoroughly until the yeast was well distributed. When gas was used, the gas injection was started simultaneously with the sulfite solution starting to drip.

The disappearance of any sugar reaction using Osts's reagent was taken as the end of the fermentation time (Fehling solution is not suitable because of the acet-aldehyde present).

Glucose was used throughout all experiments, but saccharose might have been employed with identical results. The inversion is not changed under above conditions and takes place much faster than the fermentation itself.

An oxygen fermentation with the addition of ammonium phosphate alone was finished after 72 hours. An oxygen fermentation with magnesium sulfate alone as nutrient was finished after 28 hours; and oxygen without both nutrients was completed after 28 hours, too. These fermentations were set up simultaneously, samples taken every hour starting with the 7th hour. The fermentations were set up in the incubator at 30°C.

TABLE

No.	Date	Yeast Brand	Yeast g	Yeast age	Temp °C	Ferment. Time Hrs.	Gas used	SO_4% on SO_3	CH_3CHO % on glucose	$C_3H_8O_3$
19	12/18/44	N.G.	20	Fresh	35	30*	O_2	28.8	7.6	22.0
22	1/2/45	N.G.	20	Fresh	35	26*	O_2	11.8	8.35	21.98
26	1/9/45	N.G.	6	Fresh	35	24*	air stirring	7.68	12.78	23.01
27	2/27/45	Fl.	6	Fresh	35	24*	air stirring	27.01	10.88	22.74
28	"	Fl.	6	"	35	48*	N_2	3.36	11.42	23.87
29	3/7/45	Fl.	6	Fresh	35	26*	O_2 gas stopped after 3 hrs	4.76	13.54	28.30
30	"	Fl.	6	"	35	52	None —	4.69	12.92	27.0
33	3/21/45	Fl.	6	Fresh	35	19*	O_2	12.98	10.68	28.0
34	"	Fl.	6	"	35	90	None —	4.48	13.36	27.92
35	4/3/45	Fl.	6	Fresh	35	90	None —	4.48	13.51	28.29
36	"	Fl.	6	"	35	90	None —	—	13.38	27.96
37	4/10/45	Fl.	6	Fresh	Room	20*	O_2	—	10.95	25.13
38	"	Fl.(3) added 3 g after 140 hours	6	"	Room	168	None —	—	11.93	24.93
39	4/17/45	Fl.	6	Fresh	Room	19½*	O_2	16.24	11.06	24.98
40	"	Fl.	6	"	Room	20½*	air	4.44	10.39	25.44
42	4/24/45	Fl.	6	Fresh	Room	14	O_2	13.01	10.40	26.12
43	"	Fl.	6	"	Room	15	air	3.75	7.33	26.64
44	4/30/45	Fl.	6	Fresh	Room	19¼*	O_2	—	8.97	26.23
45a	5/10/45	Piel	30	1 day	Room	25*	O_2	---	10.23	22.41
46a	"	Piel	30	"	Room	96*	None —	—	10.47	22.06
50_a	5/16/45	Piel	20	Fresh	Room	49½	None —	---	10.71	23.17
51_a	5/17/45	Piel	20	1 day	Room	26	O_2	---	9.09	22.17
52_a	"	Piel	20	"	Room	44	air	—	7.82	21.65
53_a	"	Piel	20	"	Room	49½	N_2	—	6.05	21.62
54	6/4/45	Fl.	6	Fresh	Room	18½*	O_2	---	9.6	26.52
55	"	Fl.	6	"	Room	98	N_2	—	6.61	25.22
56	"	Fl.	6	"	Room	140	None —	---	12.85	26.86
57_b	6/5/45	Fl.	6	Fresh	Room	51½*	O_2	---	9.36	26.87
58_b	"	Fl.	6	"	Room	140	None —	—	12.76	26.6

TABLE (cont'd)

a) The brewer's yeast used was washed with tap water three times, drained, suctioned off. The Buchner cake was used for the fermentations.

b) Fermentations No. 57 and 58 were set up without nutrients.

* Where the asterisk is seen in the table, the fermentation time was probably shorter. The fermentations were not observed throughout the night and therefore the time is not exactly checked.

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UNITED STATES PATENT OFFICE.

JOHN R. EOFF, JR., OF WASHINGTON, DISTRICT OF COLUMBIA.

PROCESS OF MANUFACTURING GLYCEROL.

1,288,398. Specification of Letters Patent. **Patented Dec. 17, 1918.**

No Drawing. Application filed July 21, 1917. Serial No. 181,936.

(DEDICATED TO THE PUBLIC.)

To all whom it may concern:

Be it known that I, JOHN R. EOFF, Jr., a citizen of the United States, and an employee of the Bureau of Internal Revenue, United States Treasury Department, a legal resident of the District of Columbia, residing in the city of Washington, therein, (whose post-office address is 725 Shepherd street N.W.,) have invented a new and useful Process of Manufacturing Glycerol, and have made application, by petition of even date herewith, under the act of March 3rd, 1883, chapter 142, (22 Stat., 625,) praying that Letters Patent may be granted to me therefor.

The invention herein described and claimed may be used by the Government of the United States or by any of its officers and employees in the prosecution of work for the United States, or by any person in the United States, without payment of any royalty thereon.

My invention relates to the manufacture of glycerol by fermentation of any fermentable sugar in the presence of alkali.

It is well known that ordinary yeast fermentation is usually carried on in acid reacting media, and that, in such media, a small amount of glycerol is obtained as a by-product, but this amount is so small as not to be of value commercially.

By my process I ferment solutions of fermentable sugars in such a way that up to 20 or 23% of the fermentable sugar present is transposed into glycerol. As a result of my investigations I confidently believe that these amounts can be largely increased. Among other products produced are acetic acid, alcohol and acetone.

I have used in this process pure culture yeasts of both the *Cerevisiae* and *Ellipsoideus* species, but obtain the best results from the *Ellipsoideus* variety Steinberg, or the wine yeasts, known to the trade as California wine yeasts. However, I do not wish to limit myself herein to either the specific yeasts, or sugars named, since I believe that any fermentable sugar, and any yeast capable of acclimation in an alkaline medium, will produce the same results, in kind, if not in amount.

My process is as follows:

The yeasts, of the varieties named, are first cultivated in sterile grape juice, and, when in vigorous growth, this is added to a culture medium made by boiling malt sprouts in water, filtering and condensing it to a density of 4° Balling, to which is added 20% dextrose sugar, and yeast food consisting of any of the well known solutions of inorganic salts, such as Pasteur's solution, or those used for similar purposes, and containing ammonium nitrate, potassium phosphate, ammonium phosphate, magnesium sulfate, and traces of zinc and iron salts.

When fermentation is in vigorous progress, sodium or potassium carbonate, or any equivalent, non-antiseptic alkali, is added from time to time until the total amount added to 100 c. c. equals about that which would require 19 c. c. normal hydrochloric acid for neutralization.

When the yeast in this culture medium is in vigorous action it is transferred to a larger quantity of the same medium in order to obtain a larger amount of "starter" for the final transfer to the material to be fermented. This second culture medium is also made alkaline in the same way and to the same degree as the first one, as above related.

The main liquid to be fermented for the production of glycerol is made as follows:

Malt sprouts are extracted in water gradually heated to 190° F. for one-half hour, then the resulting extract is cooled and filtered free from the residue, and brought to a density of between 1° to 4° Balling, and to this is added 18 to 20% dextrose in solution. The malt sprouts furnish albuminoids and mineral salts to the wort, which serve as yeast nutrients.

To this wort, cooled to a fermentation temperature, which I have found to range between 27° and 50° C., although the optimum temperature is 37° C., I add a small amount of sodium carbonate, or equivalent alkali to render it slightly alkaline in reaction, then from one to two per cent. of the "starter" described above, and allow fermentation to proceed, adding alkali from time to time, so that the final amount of alkali added to 100 c. c. is equivalent to about 95 c. c. normal hydrochloric acid, the temperature being maintained all the time as near as possible to 37° C. I have succeeded in conducting fermentation of such a solution, and producing glycerol, when sodium carbonate has been added to the amount of 5% of the solution, and with other alkaline reacting substances in equivalent proportions, and it seems that the amount of glycerol produced is in some proportion to the amount of alkali present in the wort, up to the limit at which the yeast is able to develop. It is not material as to the inorganic salt used to produce the alkalinity so long as it is not antiseptic in its nature, and sodium and potassium carbonates, phosphates and hydroxids may be used, but I prefer to use sodium carbonate because it is comparatively cheap and easily obtainable. I have succeeded in producing glycerol in fair amounts with calcium carbonate instead of the stronger alkalis named above.

As another material to be fermented or used as a source of fermentable sugar, I may use molasses, and find that the ordinary molasses known under the trade name of "Black strap" gives good results, although any similar substance which contains fermentable sugar may be substituted; for instance, properly purified and neutralized waste sulfite liquor. By properly purified waste sulfite liquor I mean that it shall be free from sulfurous acid, or antiseptic substances, and of the character of that used in well known processes for the manufacture of ethyl alcohol by fermentation.

I have found, however, that the best results are obtained, when using "Black strap" molasses, if the fermentation is allowed to begin in the molasses while it is slightly acid in reaction, in order that the invertase of the yeast may have opportunity to invert the sucrose present, and after the fermentation has vigorously begun to add, gradually, alkali until the limits above indicated have been attained.

The molasses should be diluted until it contains about 11% total sugar, at which dilution 20% of the sugar is changed into glycerol by my process, but I am confident that further experience will enable me to largely increase this amount.

The glycerol can be obtained from the fermented wort by any of the well known processes for removal of glycerol from liquids, but this is no part of my invention.

It is understood that the statements of amounts and specific substances made in this specification are not limiting, but simply illustrative, and that not only these specific substances and amounts and proportions, but all equivalents and modifications within the limits of the claims are included within my invention and the protection of the patent for whose issue I have petitioned.

I claim:—

1. The process of producing glycerol, which consists in fermenting a solution of fermentable sugar in an alkaline reacting medium.

2. The process of producing glycerol which consists in fermenting a solution of fermentable sugar in an alkaline reacting medium whose degree of alkalinity is maintained just short of that which will inhibit further fermentation by means of successive additions of an alkaline reacting substance.

3. The process of producing glycerol by fermentation which consists in adding a vigorously fermenting grape juice to a solution of a fermentable sugar, and, after vigorous fermentation has been established in the resulting mixture, rendering the mixture alkaline by successive additions of increasing amounts of an alkaline reacting substance until the degree of alkalinity produced is just short of that which will inhibit further fermentation, and maintaining this degree of alkalinity by continuing the addition of small amounts of an alkaline reacting substance.

4. The process of producing glycerol by fermentation which consists in adding a vigorously fermenting solution of a fermentable sugar to a solution of molasses containing a fermentable sugar, and, after vigorous fermentation has become established in the resulting mixture, rendering the mixture alkaline by successive additions of increasing amounts of an alkaline reacting substance, until the total degree of alkalinity is just short of that which will inhibit further fermentation, and maintaining that degree of alkalinity by continuing the addition of small amounts of an alkaline reacting substance.

5. The process of producing glycerol which consists in cultivating yeast in a solution of fermentable sugar until vigorous fermentation has been established, adding this vigorously fermenting mixture to a larger volume of fermentable sugar, permitting vigorous fermentation to become established in this larger amount, then gradually making this solution alkaline to the degree of alkalinity which is just short of that necessary to inhibit further fermentation, and maintaining this degree of alkalinity throughout the further course of the fermentation.

In witness whereof I have herewith set my hand on this the 21st day of July 1917.

JOHN R. EOFF, Jr.

Witnesses:
E. D. Batchelder,
C. S. Kunkle.

UNITED STATES PATENT OFFICE.

WILHELM CONNSTEIN, OF BERLIN, AND KARL LÜDECKE, OF WILMERSDORF, NEAR BERLIN, GERMANY.

PROCESS FOR MANUFACTURING OF PROPANTRIOL FROM SUGAR.

1,368,023. Specification of Letters Patent. Patented Feb. 8, 1921.

No Drawing. Application filed August 13, 1919. Serial No. 317,325.

To all whom it may concern:

Be it known that we, WILHELM CONNSTEIN, chemist, a citizen of Prussia, and residing at Fasanenstreet 27, Berlin, Germany, and KARL LÜDECKE, a citizen of Prussia and residing at Kaiser Allee 156, Wilmersdorf, near Berlin, Germany, have invented a new and useful Improvement in Processes for Manufacturing of Propantriol from Sugar; and we do hereby declare the following to be a full, clear, and exact description of the same.

In a copending application Serial Number 317,324 filed Aug. 13, 1919, a process for manufacturing propantriol from sugar by fermentation in the presence of alkaline reacting salts has been described. The present process for manufacturing propantriol consists in adding nonalkaline reacting salts *i. e.* neutral or acid reacting salts to sugar and causing the mixture to be fermented above the formation of 3% propantriol from the used sugar and until the disappearance of the sugar. As sugar we may use all sorts of fermentable sugars: saccharose, dextrose, levulose, invert sugar, maltose, molasses, etc.

As salts we may use all soluble salts having no poisonous action on yeast.

Example I.

1000 grams sugars, 900 grams crystallized ferrous-sulfate and the following nutritive salts: 8 grams ammonium sulfate, 7 grams sodium phosphate, 2 grams potassium sulfate, 7 grams magnesium sulfate are dissolved in 10 liters water and 100 grams yeast (commercial press yeast or cultivated pure races) are added. One allows the mixture to stand at about 30–35° centigrade. After 5 days the sugar has disappeared, which may be determined by the known reactions. About 125 grams propantriol, *i. e.* 12.5% from the sugar, has been formed.

For isolating the propantriol one may evaporate the mixture to a degree that the ferrous sulfate may crystallize. The uncrystallized portion of ferrous sulfate is precipitated with lime, one filtrates, acidulates the filtrate with a small surplus of sulfuric acid and evaporates until the formation of a light brown syrup which contains after filtration about 80% propantriol. One may also extract the propantriol from the evaporated syrup by means of alcohol and may decolorize the alcoholic extract by means of decolorizing carbon. After evaporation of the alcohol a yellow syrup is obtained containing about 90–95% propantriol.

The crude propantriol obtained from the fermented liquor by any suitable method known for isolating propantriol may be refined by any known method, for instance by distillation with superheated steam and, if desired by concentrating the distillate.

Example II.

1500 grams sugar, 1200 grams crystallized aluminium sulfate and as nutritive salts: 10 grams ammonium sulfate, 8 grams sodium phosphate, 4 grams potassium sulfate, 10 grams magnesium sulfate are dissolved in 15 liters water and mixed with 150 grams yeast. The further treatment may be carried out according to Example I. One obtains about 200 grams propantriol.

Example III.

1000 grams sugar, 300 grams ammonium chlorid and as nutritive salts: 10 grams ammonium sulfate, 7 grams sodium phosphate, 3 grams potassium sulfate and 8 grams magnesium sulfate are dissolved in 9 liters water and added with 100 grams yeast. After 4 days having stood at 30–35° centigrade the sugar has disappeared. The liquid contains about 75 grams propantriol. The further treatment may be carried out as in Example I.

Example IV.

1000 grams sugar, 400 grams calcium-chlorid free of water and as nutritive salts: 8 grams ammonium sulfate, 5 grams sodium phosphate, 2 grams potassium sulfate are dissolved in 10 liters water. One adds 100 grams yeast and allows to stand at 30–35° centigrade. After 6 days the sugar has disappeared and the solution contains about 85 grams propantriol. One adds to the hot liquid sodium carbonate until further additions do not cause a precipitate. Then one filters from the precipitated calcium carbonate, acidulates the filtrate with hydrochloric acid until a slight acid reaction and evaporates the liquid to syrupy consistency. The obtained magma containing sodium chlorid is extracted with absolute alcohol, the alcoholic liquid treated with decolorizing carbon and the alcohol is evaporated. The remaining light brown syrup contains 80–85% propantriol, which may be recovered by distillation with superheated steam under diminished pressure.

We claim:

A process of obtaining propantriol, comprising mixing sugar-containing solutions with water-soluble salts of non-alkaline reaction in larger amounts than sufficient to form nutrients for yeast, adding yeast, and then allowing the liquid to ferment until the sugar disappears.

In testimony whereof, we have signed our names to this specification in the presence of two subscribing witnesses.

WILHELM CONNSTEIN.
Dr. KARL LÜDECKE.

Witnesses:
Julius Franke,
Erna Wolff.

Patented Oct. 14, 1924. **1,511,754**

UNITED STATES PATENT OFFICE.

WILHELM CONNSTEIN, OF BERLIN, AND KARL LÜDECKE, OF WILMERSDORF, NEAR BERLIN, GERMANY.

PROCESS FOR MANUFACTURING OF PROPANTRIOL FROM SUGAR.

No Drawing. Application filed August 13, 1919. Serial No. 317,324.

(GRANTED UNDER THE PROVISIONS OF THE ACT OF MARCH 3, 1921, 41 STAT. L., 1313.)

To all whom it may concern:

Be it known that we, Wilhelm Connstein, chemist, a citizen of Prussia, and residing at Fasanenstreet 27, Berlin, Germany, and Karl Lüdecke, chemist, a citizen of Prussia, and residing at Kaiser Allee 156, Wilmersdorf, near Berlin, Germany, have invented a new and useful Improvement in Processes for Manufacturing of Propantriol from Sugar (for which we have filed the following applications in foreign countries: Germany, 298,593, filed April 12, 1915; Germany, 298,595, filed April 22, 1916; Germany, 298,594, filed April 22, 1916; Germany, 298,596, filed May 19, 1916; all patents are not yet published, kept secret; Germany, Ser. Nr. V. 13,860, filed June 18, 1917, are not yet granted; Hungary, Ser. Nr. 2,682, filed July 22, 1916; Hungary, Ser. Nr. 2,684, filed July 27, 1916; Hungary, Ser. Nr. 2,685, filed July 27, 1916; Hungary, Ser. Nr. 2,686, filed July 27, 1916; Hungary, Ser. Nr. 10,407/18, filed July 13, 1918, all are not yet granted; Austria, Ser. Nr. A. 3,307/16, filed July 20, 1916; Austria, Ser. Nr. 61,497, filed July 5, 1918, all not yet granted; all these patents and applications have been filed by the Vereinigte Chemische Werke Akt.-Ges. with affiants' knowledge and consent); and we do hereby declare the following to be a full, clear, and exact description of the same.

The present process refers to the manufacture of propantriol from sugar by fermentation. The formation of propantriol from sugar by fermentation has been already known. The proportion of propantriol obtained according to the hitherto known processes, is however very small, about 1–3% from the used sugar, for which reason the industrial or commercial manufacture of propantriol from sugar has been until now unpracticable. The object of the present invention is to improve the manufacture of propantriol from sugar by means of yeasts.

The present process consists in causing sugar to ferment in alkaline solution, so that the formation of alcohol is restricted and the formation of propantriol is increased above the proportion obtained in the normal fermentation, i. e., above 3% of the sugar. If one causes, as hitherto usual, sugar or starch to ferment in neutral or acid solution only small amounts of propantriol are formed, whereas acids are formed which injure the isolation of the small amounts of propantriol obtained. The formation of acids are completely suppressed or essentially diminished by the fermentation in alkaline medium.

The present process is carried out by the addition of alkaline reacting substances to the sugar solution to be fermented. Inorganic as well as organic substances of this kind may be used. It is suitable to use only substances which are not poisonous with reference to yeast.

Suitable alkaline reacting substances are for instance: ammonium phosphate, ammonium carbonate, sodium phosphate, sodium carbonate, sodium bicarbonate, sodium sulphite, sodium acetate, amine salts. One may use a single compound or a mixture of several ones. The amounts of the alkaline compounds to be used may vary.

One may add to the liquor to be fermented nutrients for the yeast.

In order to accelerate the process and increase the formation of propantriol one may add catalysts, for instance manganese sulphate, iron sulphate, magnesium sulphate and such like.

Suitable sugars are for instance: grape-sugar, glucose, fructose, inverted saccharose, maltose; saccharified starch and such like.

As yeast one may use the ordinary commercial yeast, especially pressed yeast, one may however also use cultivated pure yeast and also several races of yeast.

The isolation or separation of the propantriol may be carried out by, if desired, decolorizing the fermented liquor, concentrating the liquor and subjecting the concentrated mass to a distillation process or extracting the propantriol by means of suitable organic solvents or by any other known method, for instance by treating the original solution with inorganic salts like calcium-barium chloride, ferrous sulphate and so on. One may also separate the yeast from the fermented liquor by filtration, precipitate injuring by-products by means of lime, iron compounds or magnesia and concentrate the purified liquor, whereupon the further steps for isolating propantriol are carried out.

Example I.

200 grams sugar and 140 grams secondary sodium phosphate are dissolved in 2 litres water to which solution 50 grams commercial yeast, containing preferably lactic-acid bacterias, are added. The mixture is allowed to ferment at about 30–35° centigrade during about 40–80 hours according to the quantity and the character of the yeast employed, until the sugar has practically disappeared. Then the mixture is boiled if desired with decolorizing carbon, filtrated, and concentrated to syrupy consistency. The propantriol may be extracted by means of alcohol. After the vaporization of the alcohol one obtains a residue of propantriol, the amount of which is about 14% of the used sugar.

One may use as sugar technical sacchariferous liquids, as for instance, syrups or molasses, which one may deprive, if necessary, before the fermentation, totally or partly, from injuring substances in the known manner. One dissolves the alkaline compounds in these liquids. The addition of the alkaline compounds or the yeast may be carried out successively or all at once.

Example II.

200 grams sugar and 10 grams ammonium carbonate are dissolved in 1.5 litres water and 20 grams yeast are added. The further treatment is according to Example I. One obtains about 10% propantriol of the used sugar.

Example III.

400 grams sugar, 80 grams sodium bicarbonate, 60 grams yeast and 2 grams manganese sulphate with 3.5 litres water are caused to be fermented. The mixture is treated according to Example I. One obtains about 12% propantriol of the used sugar.

Example IV.

500 grams sugar, 20 grams sodium carbonate, 80 grams yeast and 4 litres water is caused to be fermented at 30° centigrade. One obtains after the treatment according to Example I 12% propantriol of the used sugar.

Although all alkaline substances which are not poisonous to yeast may be used the alkaline sulphites have been found especially suitable. When used in certain large proportions the alkaline sulphites produce an especially high yield of propantriol and remarkable quantities of acetaldehyde. According to our general experience the yield of propantriol seems to vary proportionally to the quantities of the employed alkaline sulphites, i. e., the more of the latter is taken the higher is the yield of propantriol.

Example V.

1 kilogram saccharose, 100 grams normal sodium sulphite and 100 grams yeast are added to 5.6 litres water, the mixture is allowed to be fermented at from 30° to 36° centigrade. The fermentation is continued until the sugar has disappeared or has practically disappeared. The formed alcohol and aldehyde are distilled off, the remaining liquid is boiled with decolorizing carbon, filtered and cencentrated. The residue is extracted with alcohol. After the vaporization of alcohol and aldehyde one obtains about 14.3% propantriol, whereas the amount of alcohol and aldehyde, distilled off before the concentration is about 39%. If one uses 120 grams sulphite in the present example one obtains about 16% propantriol and about 30% alcohol mixture, if one uses 250 grams sulphite one obtains about 23.5% propantriol and about 24% alcohol mixture and so on. It is to be noticed that the fermentation depends besides to a certain extent upon the quality and race as well as from the power of activity of the yeast employed, i. e., all these circumstances may exercise an influence on the rapidity of the reaction and on the yield of the final products.

In the place of sulphites one may use compounds which allow sulphites to form in the process, for instance a mixture of bisulphites and sodium carbonate.

It has proved suitable to use besides the sulphites in addition to them salts, which have a reducing action as for instance hydrosulphites, hyposulphites, sulphoxylates, preferably in small portions from 0.25 to 1% of the sugar.

It has been found that it is not necessary for each fermentation with alkaline substances to use fresh yeast, but that one may use yeast which has been already employed for the manufacture of propantriol in alkaline reaction, whereby it is preferable to subject the yeast to a purifying fermentation.

Example VI.

1 kilogram of saccharose, 12% sodium sulphite, 1% sodium hyposulphite, 6.6 litres water are mixed and 10% yeast are added. One obtains about 14.3% propantriol from the sugar. The yeast is separated from the liquid, washed with water and digested with diluted acid, in which treatment yeast nutrients may added. The acid reaction is gradually neutralized in order to acclimatize the

yeast to the alkaline medium. Then one uses the yeast for fermenting fresh amounts of sugar with sulphites as alkaline compounds and if desired with addition of hyposulphites. One obtains about 15.8% propantriol. After the yeast has been separated and subjected to a repeated purifying fermentation one obtains by a third use with sulphite and hyposulphite also about 16% propantriol and so on.

The amount of propantriol formed by the present invention according to the various modifications described above is increased proportionally to the strength of the alkaline reaction or the amount of the alkaline reacting substances, provided that the quantity and character of the alkaline substances used is not detrimental to the yeast, but the said increase goes only to a certain point varying according to the nature of the added substance. One may add without injuring the formation of propantriol further amounts of alkaline reacting substances by a simultaneous use of neutral salts of magnesium. The use of the said salts has been found especially effective for alkaline sulphites. Generally the formation of propantriol proceeds slowly with an addition of more than about 70 per cent as much sulphites as sugar, whereas in the simultaneous use of neutral salts of magnesium even higher amounts of sulphites may be added. Especially suitable is magnesium sulphate or magnesium chloride, but one may also use neutral magnesium salts of organic acids. Of course it is a condition that the salts are not poisonous with reference to yeast. A special advantage of the use of neutral magnesium salts is an acceleration of the fermentation.

Example VII.

1 kilogram sugar, 500 grams sodium sulphite (without crystallization water) and 250 grams magnesium sulphate are dissolved in 8 litres water and fermented with 100 grams yeast. Output of alcohol mixture about 13% and of propantriol: about 33% of the used sugar.

Example VIII.

1 kilogram sugar, 1 kilogram magnesium chloride and 750 grams sodium bicarbonate are dissolved in 7 litres water and mixed with 150 grams yeast. The mixture is allowed to stand at 30° centigrade. After about 2 days the fermentation will be finished. Output: about 23% alcohol, about 20% propantriol of the used sugar.

Example IX.

1 kilogram sugar, 1 kilogram magnesium acetate and 1 kilogram sodium sulphite are dissolved in 8 litres water and mixed with 150 grams yeast. The fermentation will be finished after about 3–5 days, whereas the fermentation until the total decomposition of sugar will last longer than 4–5 days above the indicated time, if no magnesium acetate will be present. The output is: about 16% alcohol mixture, about 35% propantriol of the used sugar.

A further modification of the process is that one adds to the fermenting mixture, preferably at the stage in which the fermentation has reached its culmination and a large portion of the sugar has been fermented new portions of sugar, with or without further addition of salts or yeast or both added. By this modification it is possible to ferment higher amounts of sugar with a certain amount of yeast and salts (sulphites, phosphates etc.) than without the modification, whereas the duration of the fermentation will be somewhat shortened.

The additions of the alkaline and neutral salts may be the same as in the beginning of the fermentation, but one may also use different additions.

Example X.

750 grams sugar, 300 grams sodium sulphite, 5 grams magnesium sulphate, 6 grams ammonium sulphate, 2 grams potassium sulphate are dissolved in 6 litres water, mixed with 75 grams fresh press yeast and allowed to stand at about 30° to 35° centigrade. After 24 hours, when the fermentation has reached its culmination a solution of 750 grams sugar, 60 grams sodium sulphite, 1.5 grams ferrous sulphate, 3 grams ammonium sulphate, 1 gram potassium sulphate, in 1 litre water and 25 grams fresh press yeast are added. After the fermentation has finished the propantriol is isolated as in the Example I or in another known manner.

We claim:

1. The process for manufactureing propantriol which consists in adding alkaline sulphites (until alkaline reaction) and yeast to sugar and then allowing the mixture to be fermented.

2. The process for manufacturing propantriol which consists in adding alkaline sulphites (until alkaline reaction) and yeast to sugar causing the sugar to be fermented in presence of alkaline sulphites, separating the yeast and adding the separated yeast and alkaline reacting substances to sugar whereupon the process is repeated.

3. The process for manufacturing propantriol which consists in adding alkaline sulphites (until alkaline reaction) neutral salts of magnesium in a higher amount than necessary as yeast nutrients, and yeast to sugar and causing the sugar to be fermented.

4. The process for manufacturing propantriol which consists in adding alkaline sulphites (until alkaline reaction) and yeast to sugar, causing a portion of the sugar

to be fermented, adding new portions of sugar and causing the sugar to be fermented.

5. The process of producing glycerol, which consists in fermenting a solution of fermentable sugar in an alkaline reacting medium.

In testimony whereof, we have signed our names to this specification in the presence of two subscribing witnesses.

DR. KARL LÜDECKE.
WILHELM CONNSTEIN.

Witnesses:
JULIUS FRANKE,
ERNA WOLFF.

Patented Apr. 18, 1939

2,154,930

UNITED STATES PATENT OFFICE

2,154,930

PROCESS FOR THE PURIFICATION OF POLYHYDRIC ALCOHOLS

Theodore Evans, Berkeley, Calif., assignor to
Shell Development Company, San Francisco,
Calif., a corporation of Delaware

No Drawing. Application December 27, 1937,
Serial No. 181,995

8 Claims. (Cl. 202—56)

The present invention relates to a process for the removal of certain undesirable constituents from polyhydric alcohols, and more particularly, to the removal of coloring bodies from glycerol.

Recent developments, such as the advent of Cellophane, synthetic resins, etc., have greatly increased the consumption and dictated new and exacting specifications for polyhydric alcohols, especially glycerol, and as a consequence, considerable attention has been given to the problem of producing these products in a pure state from new sources.

One promising solution to the problem is in the preparation of glycerol from petroleum hydrocarbons. Not only is it possible to produce glycerol from this source at a reasonable cost, but with proper care a glycerol of higher purity may be made. In this process, the crude glycerol liquor containing water, salt and glycerol is boiled down to remove the water, whereby the bulk of the salt crystallizes out and is removed. The crude glycerol containing about 80% glycerol, 8% salt and 12% water may be distilled in vacuo to yield a glycerol of high purity.

The use to which the glycerol is to be applied, however, dictates the requirements as to the purity. For example, glycerol used as a plasticizing agent in Cellophane must meet very stringent specifications and is sometimes designated as very pure glycerol. In actuality, however, the glycerol used for this purpose is exceptionally free from ash-forming, coloring and odoring impurities but often contains a considerable amount of impurities, such as trimethylene glycol, methyl glycerol, etc., which, for the purpose at hand, exert no or little detrimental effect.

On the other hand, in the manufacture of certain synthetic resins, while the requirements regarding color and odor are quite lenient, the presence of trimethylene glycol, methyl glycerol, etc., is to be avoided as far as possible.

The glycerol obtainable through proper synthesis from petroleum hydrocarbons is exceptionally free from these latter type impurities. This glycerol, however, in spite of its analytical purity, contains a trace of coloring matter, which, although far too small to be detected analytically, renders the material unfit for certain exacting uses.

An object of the present invention is to provide a method whereby these coloring bodies, whenever present, may be removed from polyhydric alcohols. A further object of the invention is to provide a method whereby glycerol of exceptional limpidity may be produced. A further object of the invention is to provide a method which is economical, which is commercial, and which can be carried into practice on an industrial scale.

These objects, I have found, may be accomplished by a suitable extraction process. According to the preferred embodiment of my invention, I extract the once fractionated glycerol with a suitable immiscible solvent at an elevated temperature. After mechanically separating the extract and raffinate phases, I subject the raffinate to a second fractionation in vacuo and recover a good yield of substantially colorless glycerol.

As is known, the crude glycerol, obtained by the concentration of the glycerol liquor, contains considerable coloring matter, varying in color from a straw yellow to almost black, depending upon the source of the glycerol liquor. This coloring matter consists predominantly of non-volatile tarry material which may be completely removed by an efficient fractionation.

I have found, however, that there also exists a smaller proportion of color-forming bodies of an entirely different nature, and it is with the removal of these latter bodies that the present invention is primarily concerned. Upon efficient fractionation of the glycerol liquor, these color-forming bodies, unlike the beforementioned bodies, are found to distill with the glycerol. Although these bodies may be concentrated to a certain extent into the first and last fractions of distillate, they cannot be even partly removed by fractionation methods without incurring great losses of glycerol.

I have found that these volatile color-forming bodies are not extracted from the crude glycerol to any appreciable extent by lipophilic solvents. They are, therefore, predominantly hydrophilic in character. However, I have found that these bodies, upon being subjected to a suitable heat treatment, become lipophilic in character and hence extractable by any of the common lipophilic solvents. The prolonged heating necessitated by a distillation under diminished pressure suffices, in general, to effect the conversion. Therefore, in accordance with the present invention, the color-forming bodies may be most conveniently extracted from the distilled glycerol. Any other equivalent heat treatment may, however, be used.

Contrary to expectation, I have found that the extraction step is ineffective if applied at ordinary temperatures. Samples of distilled glycerol, upon prolonged extraction with various solvents at ordinary temperatures, were not appreciably improved. On the other hand, I have found the extraction to be quite rapid and efficient at elevated temperatures. In general, I have found temperatures ranging from about 50° C. to about 150° C. and preferably from about 80° C. to about 150° C. to be quite satisfactory and convenient. Temperatures below 50° C. are not preferred, since at about this temperature the extraction efficiency falls off markedly. Temperatures higher than 150° C. are believed to be equally applicable, providing that the temperature is not sufficiently high to cause decomposition of the glycerol or the solvent.

The coloring bodies in the distilled glycerol, being of lipophilic character, may be extracted by any one of the numerous lipophilic solvents. A suitable solvent should, however, be stable at the temperatures employed, be immiscible in and inert to glycerol and must be easily and completely removable from the glycerol raffinate. I have found the hydrocarbons, ethers, organic esters and such chlorinated solvents as substantially fulfill the above-mentioned requirements to be efficient extractants. In order to simplify the removal of the last traces of extractant from the glycerol raffinate, it is advantageous to employ such solvents as have boiling points sufficiently lower than that of the polyhydric alcohol so as to permit convenient and complete separation by fractionation. For example, for the extraction of glycerol, solvents having normal boiling points appreciably below 290° C. and preferably below 200° C. are best suited. Examples of suitable solvents include di-isopropyl ether, hexane, glycol-dimethyl ether, heptane, iso-octane, n-octylene, diisobutylene, benzene, toluene, xylene, ethyl benzene, mesitylene, pseudo cumene, cumene, cymene, butyl acetate, cyclohexane and methyl cyclohexane.

Of the classes of available solvents I have found the hydrocarbon solvents to be particularly suitable. These solvents have in general the following desirable characteristics:

1. They are very efficient extractants.
2. They possess very little solubility for glycerol. For example, xylene at 95° C. dissolves 0.04 gm. glycerol per 100 cc.
3. They are readily obtained in sufficient purity and do not require any pretreatment such as the removal of alcohol from the commercial esters.
4. They do not form peroxides which may affect the quality of the glycerol as is the case especially with the lower boiling ethers.
5. They are in general quite stable and show no tendency to hydrolyze or react with the polyhydric alcohol.
6. They are relatively inexpensive and readily obtainable in commercial quantities.

Further, in order to avoid the necessity of carrying out the extraction step under pressure, I prefer to use solvents of the above classes having normal boiling points appreciably higher than the temperature prevailing during the extraction. It is to be understood, however, that lower boiling solvents employed under suitable pressure are also applicable.

Any traces of extractant remaining after the extraction of the coloring matter and separation of the phases may be removed by distillation, blowing with an inert gas, in vacuo, or any other of the conventional methods. Glycerol thus purified and freed from traces of extractant meets the usual specifications.

I have found, however, that by subjecting the extracted glycerol to a second vacuum distillation, a further improvement may be realized yielding a glycerol of exceptional limpidity.

Thus, after extraction there invariably remains a trace of coloring matter. Upon distilling the extracted glycerol in vacuo, it is found that this coloring matter is concentrated into the first fraction to distil. By collecting the more colored first fraction separately, and returning it to the next succeeding batch to be extracted, the main distillate is found to be practically color free, i. e., having a color of less than 10. (The color figures used throughout this specification refer to the conventional platinum-cobalt scale in which a color of 25 is designated as "water white".)

While in the preferred embodiment of my invention I subject substantially anhydrous glycerol to the extraction step, it is to be understood that the presence of water has no harmful effect on the process and is only avoided because of the high cost of its subsequent removal.

The process may be carried out either continuously, intermittently or batchwise. The solvent may be used in a single step, or in subdivisions, or countercurrent operation may be employed. A temperature gradient may be maintained, if desired.

The following examples are submitted solely to illustrate suitable executions of my invention and the effectiveness thereof, and are not to be construed as limiting the scope of the invention to the extractant, temperature, mode of execution, and the like.

Example I

A volume of crude glycerol obtained through synthesis from petroleum hydrocarbons and containing about 80% glycerol was fractionally distilled under (1–2) mm. Hg pressure, whereupon a distilled substantially pure anhydrous glycerol having a color greater than 50 was obtained. This glycerol was extracted at about 86° C. with a total of about 1.4 volumes of xylene. The glycerol raffinate was then subjected to a second fractional distillation under one mm. Hg pressure, and the first 10% to distil collected as a separate fraction. The color of the first 10% fraction was about 25, while the remaining 86.5% taken overhead had a color of 0–5. The glycerol was, moreover, very satisfactory as regards odor, taste, etc.

Example II

A volume of a very colored, distilled glycerol (color 250) was divided into two portions. Portion I was refractionated under diminished pressure. Portion II was extracted at 130° C. with 1.2 volumes of xylene in six equal portions and finally refractionated under diminished pressure. The colors of fractions of the distillates are given in Table I:

Table I

Portion I			Portion II		
Fraction	Percent of original glycerol	Color	Fraction	Percent of original glycerol	Color
1	12.6	500	1	12.5	20
2	12.7	150	2	12.1	10
3	12.6	100	3	12.1	10
4	12.6	50	4	12.1	7
5	12.5	40	5	12.1	7
6	12.5	35	6	12.1	7
7	12.5	35	7	12.4	7
8	9.3	50	8	4.0	7
			9	6.1	25

Example III

A volume of distilled glycerol having a color of 50 was extracted at 85° C. with 0.8 volume of xylene in four portions and finally fractionally distilled under diminished pressure. The colors of the various fractions are given in Table II.

Example IV

A volume of a very colored distilled glycerol was extracted at 95° C. with 1.4 volumes of isoöctane and finally fractionally distilled under diminished pressure. The colors and quantities of the various fractions are given in Table II.

Example V

A volume of alpha-methyl-glycerol was extracted at 95° C. with 1.4 volumes of xylene and fractionally distilled under diminished pressure. The colors and quantities of the various fractions are given in Table II.

Table II

Fraction	Example III		Example IV		Example V	
	Percent	Color	Percent	Color	Percent	Color
1	7.2	15	12.1		5.7	35
2	3.6	5	6.7	12	5.8	25
3	3.8	2	12.9	10	5.8	20
4	62.5	0	12.6	5	5.7	15
5	7.0	2	12.6	5	5.8	12
6	7.1	2	12.7	5	57.8	5–10
7	6.6	10	12.7	7	5.8	25
8			5.4	10	6.6	Over 50
9			6.9	12		
10			3.2			

While in the foregoing examples I have used a quantity of extractant equal to from 0.8 to 1.4 times the volume of the polyhydric alcohol, it is to be understood that the invention is not limited to these quantities. The amount of extractant preferably used depends upon the amount of the color-forming bodies present, the intimacy, method, and time of contact, etc., according to the well known laws of extraction, and may vary between wide limits.

The solvent, after use, may be easily and completely recovered for reuse. Upon subjecting the extract to a simple distillation, the solvent is completely recovered as the distillate while the color-forming bodies, accompanied by a small amount of polyhydric alcohol, remain as the residue. With the exception of the small amount of polyhydric alcohol unavoidably polymerized during the fractionation, the polyhydric alcohol in the residue from the distillation of the extract represents the only losses incurred by the treatment. (The quantity of color-forming bodies removed is too small to measure.)

While I have found the present method particularly suitable for the removal of certain color-forming bodies from glycerol, and particularly from glycerol synthesized from petroleum hydrocarbons, and have stressed this preferred application in the foregoing, it is to be understood that the invention is applicable to the treatment of other polyhydric alcohols, such as glycerol from other sources, ethylene glycol, erythritol, arabitol, mannitol, sorbitol, etc., when contaminated with color-forming bodies of the above-mentioned character.

As various modifications of my invention are possible without departing from the spirit thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim as my invention:

1. A process for the removal of coloring matter from glycerol which comprises the steps of extracting substantially anhydrous distilled glycerine with an iso-octane at a temperature of from 80° C. to 150° C., separating the extract and raffinate phases, and fractionally distilling the raffinate phase whereby a decolorized glycerol is obtained.

2. A process for the removal of coloring matter from glycerol which comprises the steps of extracting substantially anhydrous distilled glycerol with xylol at a temperature of from 80° C. to 150° C., separating the extract and raffinate phases, and fractionally distilling the raffinate phase whereby a decolorized glycerol is obtained.

3. A process for the removal of coloring matter from glycerol which comprises the steps of extracting substantially anhydrous distilled glycerol at a temperature of from 80° C. to 150° C. with a hydrocarbon which is immiscible with glycerol, separating the extract and raffinate phases, and fractionally distilling the raffinate phase, whereby a decolorized glycerol is obtained.

4. A process for the removal of coloring matter from glycerol which comprises the steps of extracting distilled glycerol at a temperature of from 80° C. to 150° C. with a hydrocarbon which is immiscible with glycerol, separating the extract and raffinate phases, and fractionally distilling the raffinate phase, whereby a decolorized glycerol is obtained.

5. A process for the removal of coloring matter from glycerol which comprises the steps of extracting distilled glycerol at a temperature of from 80° C. to 150° C. with a lipophilic solvent which is immiscible with glycerol, separating the extract and raffinate phases, and fractionally distilling the raffinate phase, whereby a decolorized glycerol is obtained.

6. A process for the removal of coloring matter from glycerol which comprises the steps of subjecting the glycerol to a heat treatment equivalent to a distillation under diminished pressure, extracting the glycerol at a temperature above 50° C., but below that at which excessive decomposition takes place, with a lipophilic solvent which is immiscible with glycerol, separating the extract and raffinate phases, and fractionally distilling the raffinate phase, whereby a decolorized glycerol is obtained.

7. A process for the removal of coloring matter from glycerol which comprises the steps of subjecting the glycerol to a heat treatment equivalent to a distillation under diminished pressure, extracting the glycerol at a temperature above 50° C., but below that at which excessive decomposition takes place, with a lipophilic solvent which is immiscible with glycerol, separating the extract and raffinate phases, and removing any trace of solvent from the decolorized glycerol.

8. A process for the removal of coloring matter from polyhydric alcohols which comprises the steps of subjecting the polyhydric alcohol to a heat treatment equivalent to a distillation under diminished pressure, extracting the polyhydric alcohol at a temperature above 50° C., but below that at which excessive decomposition takes place, with a lipophilic solvent which is immiscible with glycerol, separating the extract and raffinate phases, and removing any trace of solvent from the decolorized polyhydric alcohol.

THEODORE EVANS.

Patented Aug. 15, 1939

2,169,245

UNITED STATES PATENT OFFICE

2,169,245

GLYCEROL FERMENTATION PROCESS

Frank M. Hildebrandt, Baltimore, and Norris M. Erb, Riviera Beach, Md., assignors to U. S. Industrial Alcohol Co., New York, N. Y., a corporation of West Virginia

No Drawing. Application June 30, 1937,
Serial No. 151,178

6 Claims. (Cl. 195—38)

This invention relates to the production of glycerol by yeast fermentation of sugar solutions, with especial reference to molasses, particularly blackstrap molasses.

It is well known that alkalinization of a yeast fermentation increases the small amount of glycerol formed in the normal type of fermentation. It is also well known that glycerol production is increased if sodium sulfite is added to a yeast fermentation to combine with the acetaldehyde formed as an intermediate. Attempts have been made to utilize these possibilities in a commercial way, but up to the present time the processes used have had only a limited degree of success.

Practically all of the fermentation glycerol produced commercially has been from pure sugar solutions with nutrient salts added. The fermentation difficulties associated with blackstrap molasses added to the difficulty of recovery of the glycerol have prevented any extended use of molasses as a raw material. This has been the case in spite of its low cost as a source of sugar. Processes for the production of glycerol by fermentation have not only had to use pure sugar, but very large amounts of yeast have been used, so large that this becomes one of the most costly ingredients of the mash.

Various procedures have been proposed utilizing sulfite, soda ash or other alkalinizing agents, one or more, but with blackstrap molasses as a raw material, difficulty is met in operating them. The fermentation is, for instance, materially slowed down by alkali additions, thus introducing an infection hazard in plant operation. Overdoses of alkalinizing substances frequently stop the fermentation permanently, making it difficult or impossible to salvage the sugar, which involves considerable loss.

The degree of sensitivity to doses of alkali varies from run to run. Therefore, even if the method of adding the alkali is kept the same, one cannot be sure the fermentation will give a constant result. Such uncertainty renders the ordinary alkaline fermentation procedure of little practical value since it may be so readily upset by slight irregularities necessarily associated with large-scale operation.

We have found that the disadvantages noted may be overcome by taking account of the fact that they are all related to interference with the cell multiplication phase of the fermentation. Therefore, if one can conduct the fermentation so that all or the major portion of the yeast cells which will be required to effect the fermentation is pre-formed before the addition of the alkalinizing agent or agents, the subsequent enzymatic conversion of sugar to alcohol and glycerol will proceed at a rapid rate.

This has been accomplished by the application of the fermentation process described in our co-pending application Serial No. 151,177 to a substrate modified by the addition of an agent having the property of increasing the glycerol-alcohol ratio. The improvement includes the growing of a yeast crop in an aerated low-sugar mash, preferably in a medium consisting of still residue from a previous ethyl alcohol fermentation containing about 1.5 grams of residual sugar per 100 cc. This crop is obtained by seeding the slop or still residue with a small quantity of yeast, say 0.1% to 2% by volume. The seeded mash is then aerated from 12 to 20 hours or as long as is necessary to produce maximum yeast growth. Nutrients such as phosphates, ammonia, ammonium salts, etc. may be added if desired to promote the yeast growth. When the crop has been developed, sugar in the form of molasses or other fermentable material is added in sufficient quantity to increase the sugar concentration to between 15–20 grams per 100 cc. Aeration is then discontinued and the glycerol-alcohol phase of the operation begins. When the fermentation is gassing vigorously, which in this type of fermentation takes from 15 minutes to one hour after the sugar concentration has been adjusted, the alkalinization or sulfite treatment may be begun. We have found, for instance, that a quantity of a suitable alkali as high as 40% of the sugar in the mash may be added in a single dose. When such an amount is added to a yeast fermentation as usually carried out, it has to be divided into several doses and very painstaking control must be practiced in order to avoid complete stoppage of the fermentation.

The following illustrations bring out the greater tolerance of the improved process for large doses of alkaline salts such as sodium carbonate and sodium sulfite.

Type of seeding	Percent Na_2CO_3 sugar basis	Percent glycerol on sugar basis
4%—standard	40 (single dose)	5.1
Pre-grown yeast crop	40 (single dose)	17.3

Type of seeding	Percent sodium sulfite sugar basis	Percent glycerol on sugar basis
4%—standard	32.6 (single dose)	15.7
Pre-grown yeast crop	32.6 (single dose)	20.3

It is to be understood that neither one of the above examples is given as an illustration of the optimum conditions for glycerol production but simply as illustrations of the greater sensitivity of fermentations in which cell multiplication is required to take place in the presence of high sulfite and hydroxyl-ion concentration. We do not, for instance, recommend adding the alkaline salts in a single dose if the best results are to be obtained in the glycerol fermentation. Addition at intervals is to be preferred, but our improved process avoids the hazard of stopping the fermentation by an overdose of alkali. Best results are obtained by so regulating the addition of one or more alkalinizing agents in the second stage of the process, as by adding these agents in successive portions, that the pH of the mash of the second stage of the process is kept below 9.0 throughout this stage. Any suitable non-toxic alkalinizing agent having the property of causing an increase in the production of glycerol may be employed, for example, sodium carbonate, potassium carbonate, sodium sulfite, potassium sulfite, ammonia, and the like.

A special advantage lies in the use of still waste (or slop) from a previous ethyl alcohol fermentation as the medium for the yeast building stage, on account of the fact that this waste provides sugar for the reproductive phase of the yeast. A further advantage arises from the presence of salts in the spent waste. There is definite indication in the literature and in practice that high concentrations of any non-toxic salts increase glycerol production. There is also an advantage in that the solids present in the slop materially increase the buffer capacity of the second stage of the fermentation. Thus, it is easier to maintain the desired hydroxyl-ion concentration, with a consequent saving in materials used for alkalinization. In the highly buffered medium, large salt additions do not bring about a harmful degree of alkalinity.

The benefit obtained by the use of a yeast crop grown in spent waste containing approximately 1.5 grams per 100 cc. sugars is shown in the following illustration. A yeast crop grown in a dilute molasses mash containing approximately the same amount of sugar as the spent waste but lacking the buffer solids is used as a basis of comparison. The alkaline material used here was soda ash and the sugar concentration was built up in the manner described above after growing the yeast and before adding the alkali.

Growing medium for yeast crop	Percent alkaline salt sugar basis, added in one dose	Percent glycerol on sugar basis
Dilute molasses mash	10	8.5
Spent waste	10	14.9
Dilute molasses mash	20	12.7
Spent waste	20	18.6
Dilute molasses mash	30	4.7
Spent waste	30	19.8

It will be noted from the above that there is an increase in the yield of glycerol when yeast grown in spent waste is used. Furthermore, the increased buffer capacity of the spent waste is seen to be especially effective when the amount of alkalinizing salt is increased to 30%. This amount resulted in over-alkalinization where the yeast crop was grown in dilute unbuffered molasses but not in the yeast grown in spent waste with its high content of buffering materials.

We have found that all alkalinizing substances as well as sodium sulfite interfere with cell multiplication when a critical concentration is reached. Our process, involving as it does the growing of a sufficient number of yeast cells to complete the enzymatic conversion of the carbohydrate in the final fermentation, may obviously be used with advantage regardless of the alkalinizing agent employed.

While the advantages of the invention are most pronounced when slop from an ethyl alcohol fermentation is used to form practically all or at least a large part of the mash for the yeast crop growing stage of the process, and molasses, either diluted or undiluted to bring up the sugar concentration for the second stage of the process, other materials may be used. Thus, if the aerated first stage mash is dilute molasses or other dilute sugar solution, the advantage will remain that all or most of the yeast crop will be grown in a favorable medium and under favorable conditions, whereas if the yeast multiplication and the fermentation were carried out in one step in a relatively high sugar medium the operation would be less economic. The use of blackstrap for raising the sugar content of the mash preparatory to the true fermentation stage is desirable because of the low cost of the molasses, but other sugar-containing materials may be employed for the purpose.

An example of practical procedure under the process is as follows:

541 gallons of still residue from an ethyl fermentation was cooled to 90° F. and put in a clean fermentation tank and 2 lbs. of ammonium sulfate was added. This mash was seeded with 1 gallon of active yeast and aerated for 16 hours. At this time examination under the microscope showed a large number of actively budding yeast cells, and molasses was added to the tank so as to bring the volume up to 661 gallons, with a sugar concentration of 15.9 grams per 100 cc. 150 lbs. soda ash was added in six 25-lb. doses over a period of 36 hours, and the fermentation was allowed to go to completion. It was analyzed at 63 hours and gave 124 lbs. of glycerol and 289 lbs. of alcohol.

We claim:

1. A process for the production of glycerol and ethanol by yeast fermentation, which comprises seeding a mash of low sugar content with yeast, aerating this mash until substantially all the yeast crop for the glycerol-ethanol fermentation is grown, then greatly increasing the sugar content of the mash, stopping the aeration, and carrying the glycerol-ethanol fermentation to completion in the presence of an agent having the property of causing an increase in the glycerol-ethanol ratio, which agent is introduced into the mash after substantially all the yeast crop has been grown.

2. A process for the production of glycerol and ethanol by yeast fermentation, which comprises seeding a mash of low sugar content with yeast, aerating this mash until substantially all the yeast crop for the glycerol-ethanol fermentation is grown, then greatly increasing the sugar content of the mash, stopping the aeration, and not until after substantially all the yeast crop has been grown and vigorous fermentation has set in, adding an agent having the property of causing an increase in the ratio of glycerol to ethanol produced by the fermentation.

3. A process for the production of glycerol and ethanol by yeast fermentation, as set forth in claim 1, wherein the mash of low sugar content in which the yeast crop is grown consists largely of still residue.

4. A process for the production of glycerol and ethanol by yeast fermentation, as set forth in claim 1, wherein following the growth of the yeast

crop, the sugar content of the mash is increased by the addition of molasses.

5. A process for the production of glycerol and ethanol by yeast fermentation, as set forth in claim 1, wherein the growth of the yeast crop is carried out in a mash consisting largely of a molasses fermentation still residue, and after the growth of the yeast crop, molasses is added to the mash to provide sugar for conversion to glycerol and ethanol.

6. A process for the production of glycerol and ethanol, as set forth in claim 1, wherein the sugar content of the mash is increased to over 15 grams of sugar per 100 cc. of mash.

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2,189,793

UNITED STATES PATENT OFFICE

2,189,793

PRODUCTION OF GLYCERIN BY FERMENTATION

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No Drawing. Application October 27, 1937, Serial No. 171,343. In Germany October 31, 1936

2 Claims. (Cl. 195—38)

The formation of glycerin by fermentation of sugars with yeast (top-fermentation culture-press yeast) is a process which has long been known. It is also known in the art that the output of glycerin can be considerably increased by the addition of certain steering substances to the fermenting materials, the fermentation process being in other words led in the direction of glycerin fermentation. Various salts such as phosphates, carbonates and sulphites in various concentrations have been successfully used as the addition. It has at the same time been found that with increased addition of salt the yield increases; but against this the time of fermentation in this case is considerably increased.

Owing to the relatively small yield of glycerin and owing to the long time of fermentation, processes for the production of glycerin by fermentation have hitherto had considerable drawbacks. In addition to the long time of fermentation and the poor actual yield of glycerin as compared with the theoretical yield, the further drawback which has proved of paramount importance as regards the economic practice of the glycerin fermenting process in question, has been encountered that the yeast in general only permitted a single fermentation to be carried out and that repeated use without further measures was practically impossible.

It has now been found that the above difficulties can be overcome if the energy supply system of the yeast is widened by providing for energetic respirations in addition to the fermentation.

The conditions are as follows:

In normal alcoholic fermentation, the sugar is practically quantitatively split up into alcohol and carbon dioxide, the highest possible fermentation energy being thereby put at the disposal of the yeast.

In "glycerin fermentation" the normal functioning of the yeast is hindered by the considerable addition of salt, which leads to degeneration phenomena and lower fermentation yields.

The disadvantages can be avoided if provision is made for energetic respiration of the yeast by the addition of air practically during the whole glycerin fermentation process; so much energy is thereby supplied to the yeast that the damage is compensated and the yeast remains continuously in a healthy condition. This results in an increased yield of glycerin, a more rapid fermentation and the possibility of a repeated use of the same pitching yeast. During the aeration, the oxidation can additionally be furthered by small additions for example of manganese or iron salts, which in themselves are known as oxidation catalysts for accelerating fermentation processes and for increasing the yield.

A feature which is of primary importance in the present process is that the aeration is carried out practically during the whole of the fermentation, because only thereby is the energetic respiration of the yeast which is aimed at and necessary, achieved.

In the production of glycerin by fermentation in processes which work with quite small quantities of free sulphurous acid, in the past small quantities of air have been added quite at the end of the fermentation, air being blown in in a coarse fashion or the practically fully fermented liquid being poured out; the purpose of this treatment was to hinder conversion of residues of sulphurous acid into hydrogen sulphide by the reductases of the yeast.

The above described effects and technical advantages are not achieved by this weak aeration right at the end of the fermentation, for the coarse and limited addition of air right at the end of the fermentation does not suffice to compensate the harm to the yeast and the resulting changed conditions of life occasioned by the addition of steering substances in "glycerin fermentation" and to further respiration to the degree which is achieved by aeration during the whole period of fermentation and which is necessary to attain the desired effects.

Fine aeration practically during the whole period of fermentation has been found particularly desirable, because particularly intensive encouragement of respiration is thereby obtained; methods and apparatus for fine aeration of fermenting liquids such as those of Stich, (see for example Patents Nos. 1,792,450 and 1,959,554), and so forth are in themselves so well known in the art that no further description is necessary here. The term "fine aeration" used in the claims is to be understood in this sense.

Example I

To a fermenting batch of 100 gms. of sugar, 2 gms. of ammonium phosphate, 1 gm. of magnesium sulphate and 10 gms. of top fermentation yeast race M of the Institut für Garungsgewerbe, Berlin, in 1 liter of water, 50 gms. of sodium sulphite are added in portions. Air is supplied by an aeration candle (porous ceramic body), the reaction mixture tested from hour to hour for sulphurous acid and the hydrogen ion concentration held constant within certain limits. If the reaction proceeds towards the neutral, correction must be effected by the addition of alkali. Considerable variations often occur in the individual hours. With this method after about 8 hours the sugar is used up and the glycerin can be recovered from the fermented liquid in manner known per se. In the process according to the invention the yeast shows a fairly good increase and the separated yeast is in good physiological condition so that it can be used straight away for the next fermentation.

The yield of glycerin amounts to 25–30% calculated on the sugar used.

In a test fermentation carried out without addition of air, the fermentation was finished after 72 hours and the yeast was in such a bad physiological condition that direct further use for the next fermentation was impossible; the yield of glycerin amounted to 19%.

Thus in the process according to the invention, along with an increased yield and the recovery of reusable yeast, the fermentation proceeds about nine times as fast as in the old process.

Mould yeast and especially the genera Mycoderma, Pichia, Willia and Torula have been found particularly suitable for "glycerin fermentation."

Example II

100 gms. of sugar (cane sugar or corresponding quantities of molasses or wood sugar) are dissolved in 600 c. c. of water and 2 gms. of ammonium phosphate and 1 gm. of magnesium sulphate added. After addition of 10 gms. of mould yeast (Mycoderma No. 12 of the Institut für Garungsgewerbe, Berlin) provision is made for abundant air supply, air being allowed to enter at the bottom of the vessel in finely divided form. 50 gms. of anhydrous sulphite dissolved in 400 c. c. of water are now added continuously over a period of 20 hours. After 23 hours fermentation at 34° C. the sugar is used up, whereupon the glycerin can be recovered in known manner. Yield, 30–34 gms. glycerin calculated on the sugar used.

It is clear that the yield of glycerin is increased as compared with the use of top fermentation yeast race M according to Example 1. This yeast also is in good physiological condition so that its direct further use for the next fermentation is possible.

The new process is advantageous for every glycerin fermentation process in which a weakening of the micro-organism in its life-functions occurs through the addition of steering substances.

What I claim is:

1. In the process of producing glycerin by fermentation of sugar by means of a yeast selected from the genera consisting of top fermentation culture-press yeast, Mycoderma, Pichia, Willia, and Torula, in the presence of steering substances which produce an increased yield of glycerin in the fermentation, the step which consists in effecting aeration practically during the whole period of fermentation in such a manner as to provide for energetic respiration of the yeast.

2. In the process of producing glycerin by fermentation of sugar by means of a yeast selected from the genera consisting of top fermentation culture-press yeast, Mycoderma, Pichia, Willia, and Torula, in the presence of steering substances which produce an increased yield of glycerin in the fermentation, the step which consists in effecting fine aeration practically during the whole period of fermentation in such a manner as to provide for energetic respiration of the yeast.

HUGO HAEHN.

Patented Aug. 7, 1945

2,381,052

UNITED STATES PATENT OFFICE

2,381,052

GLYCEROL FERMENTATION PROCESS

Howard M. Hodge, Linthicum Heights, Md., assignor, by mesne assignments, to U. S. Industrial Chemicals, Inc., a corporation of Delaware

No Drawing. Application February 13, 1940, Serial No. 318,705

6 Claims. (Cl. 195—38)

It is well established that sulfites, bisulfites, alkaline carbonates, molasses ash and other alkaline materials, when added to a yeast fermenting sugar solution so as to produce an alkaline mash, increase the yield of glycerol above that obtained in the normal alcoholic fermentation.

It is also generally conceded that it is desirable to employ relatively cheap sources of sugar, such as molasses, if fermentation glycerol is to compete with glycerol obtained by other processes.

A disadvantage inherent in the majority of previously described glycerol fermentation processes is the large amount of salts or alkalies required to obtain a commercially valuable glycerol yield. If, for example, a mash containing 100 tons of sugar were fermented by the soda ash process of Eoff, or the sulfite process of Connstein and Lüdecke, over 30 tons of salts would have to be added to the fermenter. If the molasses-ash process as described by Lawrie were used, over 50 tons of molasses ash would be required. The use of such large quantities adds so materially to the costs and difficulties of these processes as to render them impractical.

In general, previously described glycerol fermentation processes have called for an alkaline reacting mash. The use of an alkaline mash greatly increases the infection hazard—an item of considerable importance in plant operation. If the usual practice is followed and highly alkaline materials are added at intervals to the mash, yeast activity is stopped upon each addition. Usually it takes from two to three hours after each addition for the yeast to recover. During these periods there is an excellent opportunity for contaminating organisms to develop. Furthermore, this sharp interference with the normal yeast activity makes the fermentation precarious and thus requires close control. It would, therefore, be a distinct advantage to utilize an acid medium for glycerol production and especially advantageous if a continuous, uninterrupted fermentation were to ensue.

Glycerol production above about 3%–4% of the sugar fermented in an acid medium, except for a proposal involving a large quantity of neutral salts, has never been anticipated. Connstein and Lüdecke in U. S. Patent No. 1,511,754, page 1, lines 52–57, state: "If one causes, as hitherto usual, sugar or starch to ferment in neutral or acid solution only small amounts of propantriol are formed, whereas acids are formed which injure the isolation of the small amounts of propantriol obtained." In a similar vein, Lawrie in his monograph, "Glycerol and the glycols," states on page 130, line 6: "Normally—i. e., at pH 6.8 to say pH 3.5, 91% to 94% of the sugar fermented undergoes the usual Gay-Lussac reaction, while glycerol is formed to an amount representing 3% to 4.5% of the sugar."

It has now been found that glycerol is formed in greatly increased amounts by yeast in fermenting solutions if the pH is maintained between pH 6.0 and pH 7.0, and preferably between pH 6.4 and pH 7.0, in the presence of ammonium compounds in an amount considerably above that required for nutrition of the yeast. It becomes unnecessary to maintain the pH on the alkaline side and furthermore a small concentration of ammonium ions suffices for the function of this agency in the desired increase in glycerol.

As sources of ammonium ions or ammonium compounds in the mash, ammonia gas, aqua ammonia, and in general the ammonium salts that are non-toxic to yeast (ammonium chlorid, ammonium sulfate, ammonium phosphate, ammonium carbonate, for example) are suitable, and one or more of these agents may be employed. The quantity of such material should be limited; otherwise there is likelihood of diminished glycerol formation or even of failure of the fermentation. On the other hand, the amount of ammonia or its equivalent added to the mash is in excess of that which would be adequate solely for yeast-nutrition in a commercial fermentation. To keep the fermenting mash solution within the stated pH range any non-nitrogenous neutralizer, non-toxic to yeast, for example, lime, may be used. The additions of ammonia, gaseous or aqueous, or ammonium salts, one or more, are to be within such amounts that the ammonia equivalent is between 0.1% and 1.0%, and preferably between 0.2% and 0.5%, by weight of the mash. If 30% aqua ammonia is used the optimum amount thereof is approximately 1.0% by volume of the mash, the NH_3 equivalent being 0.3%. Since the amounts of ammonia or its equivalent and lime or its equivalent are small, the disadvantage of loading the fermentation with large amounts of salts is overcome.

In carrying out this fermentation it is advantageous, though not absolutely essential, to employ the two-stage glycerol operation described by F. M. Hildebrandt and N. M. Erb in U. S. Patent No. 2,169,245, dated August 15, 1939.

In general outline, the preferred mode of carrying out the instant invention is as follows:

A yeast crop is grown by aeration in a dilute sugar mash, preferably a still residue from a previous ethanol or glycerol fermentation. After a good yeast crop has developed (12–24 hours), molasses is added to raise the sugar content of the mash to 15–20 grams per 100 cc. Fermentation sets in promptly, and then sufficient aqua ammonia is added to bring the pH of the mash to 6.5–6.8. As the fermentation continues, hydrated lime is added when necessary to maintain the pH of the mash between 6.0 and 7.0.

Although the ammonium salts may be used, it is preferable to use aqua ammonia. The aqua ammonia or its equivalent as used in this fermentation supplies ammonium ions or ammonium compounds for increased glycerol production. The small amount used has a stimulating action in the fermentation, and thus enables one to employ a higher sugar concentration than would otherwise be permissible. Since the fermented-out mash is already acid, it is necessary, before distilling off the ethanol, only to acidify it slightly to pH 6.0 if it has not reached this point. At pH 6.0 the ammonia is non-volatile during the distillation and does not contaminate the alcohol distillate.

Any neutralizer other than lime that is non-toxic to yeast may be employed to keep the fermenting mash at the desired pH, examples being dolomitic lime, soda ash, alkaline oxides and hydroxides such as those of sodium and potassium, and alkaline carbonates such as the carbonates of potassium and sodium. Lime is preferred because of its strength as a neutralizer, its cheapness and availability. When lime is used its solubility is increased by the ammonia or ammonium salts.

The following examples illustrate the invention:

(#1) 550 gallons of still residue from a previous ethanol fermentation were put into a clean fermenter, cooled to 90° F., and 2 lbs. of ammonium sulfate were added as a yeast nutrient. The mash was then inoculated with 2 gallons of active yeast culture and aerated for 17 hours. Microscopic examination at this time showed that a good yeast crop had developed. 166 gallons of molasses were then added over a period of two hours to give a sugar concentration of 20.25 grams per 100 cc. Aeration was then discontinued and fermentation started immediately. 5 gallons of 30% aqua ammonia were then added, which changed the mash from pH 5.80 to 6.80. After 26½ hours 5 lbs. of freshly slaked lime in three gallons of water were added, raising the pH from 6.49 to 6.70. At 30½ hours a second quantity of 5 lbs. of lime was added, changing the pH from 6.46 to 6.66. At 31½ hours a third dose of 5 lbs. of lime was added which brought the pH from 6.50 to 6.70. The fermentation was then allowed to go to completion with no further additions, fermentation being complete at 70 hours at pH 6.07. Analysis showed 2.66 grams of glycerol and 6.99 grams of ethanol per 100 cc. The lime used amounted to 1.25% of the sugar contained in the molasses used.

#2) A yeast crop was grown in 525 gallons of still residue by aeration as described in Example #1. After 18 hours aeration 179 gallons of molasses were added over a period of 2½ hours to give a sugar concentration of 20.51 grams per 100 cc. Aeration was discontinued and 7 gallons of 30% aqua ammonia were then added, raising the pH from 5.6 to 6.66. At 22, 24, 29 and 35 hours separate doses each of 5 lbs. of freshly slaked lime in 3 gallons of water were added to maintain the pH of the mash between 6.60 and 6.90. Fermentation was then allowed to go to completion with no further additions and was complete at 69 hours at pH 6.48. Analysis of the beer showed 3.38 grams of glycerol and 7.03 grams of ethanol per 100 cc. The lime used amounted to 1.66% on the sugar basis.

It is not necessary to perform this fermentation in two stages, as the following example will show. However, if the two-stage process is not used, the mash should be pastuerized in order to get the best results. This adds to the cost of operation.

(#3) A mash consisting of 350 gallons of still residue from a previous ethanol fermentation, 175 gallons of molasses, and 202 gallons of water, was pastuerized, cooled and seeded with 2 gallons of active yeast culture. This mash contained 20.00 grams of sugar per 100 cc. After 18 hours, fermentation was vigorous and 7 gallons of aqua ammonia were added, changing the pH from 5.70 to 6.75. At 26 and 37 hours 5 lbs. of freshly slaked lime in 3 gallons of water were added, maintaining the pH of the mash between 6.51 and 6.90. The mash was then allowed to ferment out with no further additions and was complete at 89 hours at pH 6.44. The beer contained 3.42 grams of glycerol and 5.96 grams of ethanol per 100 cc. The lime used amounted to .84% of the total sugar.

To illustrate the use of an ammonium salt in place of ammonia and a non-nitrogenous neutralizer other than lime, the following is given:

(#4) 800 cc. quantity of still residue from a previous ethanol fermentation of molasses was inoculated with 5 cc. of an active yeast culture and aerated for 16 hours. At this time a large number of active yeast cells had developed, and 300 grams of blackstrap molasses was added, giving a sugar concentration of 17 grams per 100 cc. To this mash of 1 liter volume there were added 5 grams of technical ammonium chlorid as a source of ammonium ions. Fermentation set in promptly and 10 grams of soda ash were added, changing the pH of the mesh from 5.8 to 6.8. At 23 hours 5 grams of soda ash were added and at 30 hours 3 grams to keep the pH between 6.5 and 6.9 The mash was then allowed to ferment out with no further additions and was complete after 5 days at pH 6.35. Analysis showed 2.66 grams of glycerol and 5.38 grams of ethanol per 100 cc. of beer. The soda ash used amounted to 10.6% of the total sugar.

While it is preferable to employ non-nitrogenous neutralizers in maintaining the critical pH range, this is not absolutely essential, since fair glycerine yields can be obtained under the invention by using a non-toxic alkaline ammonium compound, in sufficient quantities, both as a source of ammonium ions and as a neutralizer to substantially keep the pH within the values stated. This may be accomplished, for example, by the addition, or additions, of ammonium carbonate in total amount approximating 10% on the sugar basis, without the addition, also, of a non-nitrogenous neutralizer.

Since the still residue obtained after distillation of the beer to remove the alcohol obtained in the herein described glycerol fermentation process is acid, and contains no toxic salts, it may be used to "slop back" in a second glycerol fermentation. When diluted with water the glycerol still residue may be used as a medium to grow the yeast required for a second glycerol fermentation. In this way part of the residual sugar from the first fermentation can be utilized, a saving in evaporating costs realized, and the glycerol carried over from the first fermentation is added to that formed in the second fermentation. In this manner the glycerol content of the beer can be gradually increased to a higher level by "slopping back" of glyecrol-containing still residue. For example, 1500 cc. amount of still residue from a glycerol fermentation made by the process here described and containing 3.04 grams of glycerol per 100 cc. was diluted with water to 3000 cc., inoculated with 10 cc. of active yeast culture and aerated for 16 hours. Microscopic examination at this time showed the presence of a large number of yeast cells. Sufficient blackstrap molasses was then added to give a sugar concentration of 19 grams per 100 cc. Fermentation set in promptly and 1% of the mash volume (38 cc.) of aqua ammonia was added, bringing the pH of the mash from 5.80 to 6.80. Small amounts of freshly slaked lime were then added at intervals to maintain the pH of the mash between 6.4 and 6.9. Analysis after 5 days showed 4.48 grams of glycerol and 5.85 grams of ethanol per 100 cc.

Whether the process is worked as a one-stage or a two-stage operation, the control of the pH of the mash is essential. Experience indicates that the optimum range is pH 6.4–pH 7.0.

From the foregoing it will be evident that this new process for glycerol fermentation has certain unique and desirable advantages. Thus, the fermentation is carried out in an acid mash, whereby the infection hazard is greatly reduced. The glycerol promoting agents—ammonia or ammonium salts and lime or the like—are required in low concentrations. Because of the small amounts of neutralizers required, the yeast cells are not subjected to drastic changes in pH, fermentation is not arrested upon each addition and a continuous uninterrupted fermentation ensues. The glycerol content of the beer can be increased to a higher level by slopping back of the non-toxic glycerol-bearing still residue.

I claim:

1. Process for carrying out uninterrupted yeast fermentation of sugar solutions, which is characterized by addition of material of the group consisting of ammonia and ammonium salts non-toxic to yeast in amount sufficiently in excess of the nutrient requirements of the yeast to promote the formation of glycerol, and maintenance of the pH of the fermentation solution between pH 6 and pH 7 by addition of one or more non-toxic neutralizers.

2. Process for carrying out uninterrupted yeast fermentation of sugar solutions, which is characterized by addition of material of the group consisting of ammonia and ammonium salts non-toxic to yeast in amount sufficiently in excess of the nutrient requirements of the yeast to promote the formation of glycerol, the amount added of such material being equivalent to 0.1%–1.0% NH_3, and maintenance of the pH of the fermentation solution between pH 6 and pH 7 by addition of one or more non-nitrogenous non-toxic neutralizers.

3. Process for carrying out uninterrupted yeast fermentation of sugar solutions, which is characterized by addition of material of the group consisting of ammonia and ammonium salts non-toxic to yeast in amount sufficiently in excess of the nutrient requirements of the yeast to promote the formation of glycerol, and maintenance of the pH of the fermentation solution between pH 6 and pH 7 by addition of lime.

4. Process for carrying out uninterrupted yeast fermentation of sugar solutions, which is characterized by addition of aqua ammonia in such amount that the NH_3 equivalent thereof is between 0.1% and 1.0% by weight of the mash, to promote the formation of glycerol, and maintenance of the pH of the fermentation solution between pH 6 and pH 7 by addition of lime.

5. A glycerol fermentation process, which comprises growing a yeast crop in a low sugar mash with aeration, greatly increasing the sugar concentration of the mash and discontinuing aeration, adding material of the group consisting of ammonia and ammonium salts non-toxic to yeast in amount sufficiently in excess of the nutrient requirements of the yeast to promote the formation of glycerol, and maintaining the pH of the fermentation solution between pH 6 and pH 7 by addition of one or more non-toxic neutralizers.

6. The process as characterized in claim 5 in which the low-sugar yeast growing mash comprises still residue from a previous yeast fermentation.

HOWARD M. HODGE.

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UNITED STATES PATENT OFFICE

2,388,840

GLYCEROL PRODUCTION

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No Drawing. Application June 23, 1941, Serial No. 399,416

7 Claims. (Cl. 195—38)

This invention relates to a process for the production of glycerol. More specifically it embraces a process for the production of glycerol by means of the fermentation of sugars.

Heretofore the principal source of glycerol has been from fats, chiefly from the unsaponifiable residue from soap-making. Although a number of fermentation processes for glycerol production have been discovered, none has been sufficiently economical to compete with soap residue glycerol except in time of war.

When fermentable sugars are acted upon by yeasts, under normal acid conditions, the resultant is primarily ethanol and carbon dioxide, accompanied by the formation of small amounts of glycerol and acetic acid. It is necessary to change the equilibrium of the fermentation in order that substantial yields of glycerol be obtained.

Two general methods have been advanced for glycerol production by fermentation processes. The first of these is the "sulfite fixation" process, in which sufficient of a soluble sulfite is added to the fermentation to cause the fixation of acetaldehyde and the consequent formation of glycerol. Except as noted below, all of these fermentations were carried forward in an alkaline medium unfavorable to the growth of yeasts and the resulting glycerol was difficult to separate from the soluble sulfite or other salts remaining. Both of these difficulties were claimed to be obviated in a sulfite fixation process calling for the addition of sulfur dioxide as an acetaldehyde fixative, but concentrations of sulfur dioxide sufficient for useful conversions to glycerol are toxic to yeasts. The second general method is the "alkaline fermentation" process, in which the fermentation is carried out in a medium made alkaline by the addition of alkali salts or bases. The same difficulty of separating the glycerol from the alkali compounds arises as in the sulfite fixation procedure. The alkaline environment is unfavorable to the development of yeasts and is favorable to the growth of certain kinds of bacteria. In addition, various contaminating by-products are often formed. The separation problem is not present in the process which alkalizes with ammonia, but the claimed yields are insufficient to be commercially attractive.

We have discovered a method of producing glycerol by the fermentation of fermentable sugars in which these difficulties noted above have been obviated and from which satisfactory recoverable yields are obtainable.

It is an advantage of our process that the conversion of the sugar used into useful products, including glycerol, is practically complete and that the recovery of each of them in pure form is a very high proportion of that produced. The fermentation products consist of acetaldehyde and glycerol, which are produced in direct proportion to each other, and ethanol, which is produced in inverse proportion to the first two.

A further advantage of our process is that virtually complete recovery of additions to the fermentation is possible in a form in which they can be reused in the process.

Broadly speaking, our new and improved process comprises the fermentation of fermentable sugars in an acid environment in the presence of slightly soluble sulfites.

The raw material for our process is any fermentable sugar or mixture of such sugars, either in pure form or combined with other substances, as in molasses, syrup, etc. For proper action by the yeasts it is necessary that the sugar be in solution. Concentrations of sugar as high as 25 g./100 ml. may be used, although more rapid fermentations will be obtained if the concentration does not exceed 20 g./100 ml. Weak concentrations unduly dilute the end products and make recovery difficult.

To the sugar solution we add an excess of some slightly soluble sulfite. By "excess," as used herein and in the appended claims, is meant sufficient so that a portion always remains undissolved. If insufficient sulfite is added in the first instance, more may be added at any time during the process. The purpose of the sulfite, as will hereinbelow more fully appear, is to supply a source of bisulfite ion whereby the acetaldehyde formed will be fixed. We have found that if the solubility of the sulfite used is above about 2 parts in 100 parts of cold water, the formation of bisulfite ion will be so great as to be toxic to yeast if the pH of the solution is adjusted to a point favorable to yeast growth. Therefore, as used in this specification and the appended claims, the term "slightly soluble sulfite" means salts having a solubility of less than 2 parts in 100 parts of cold water (including so-called insoluble salts), having the sulfite for a negative radical, and having a positive radical which is substantially non-toxic to yeasts in the concentrations used.

We prefer to use calcium sulfite or magnesium sulfite as a slightly soluble sulfite in our process since they are relatively cheap, easily obtainable, and positive ions are not only non-toxic but actually beneficial to the growth of yeasts.

In the above mixture we introduce sufficient yeast for rapid fermentation. Since the presence of sulfite initially retards the action of yeast, we prefer to use acclimatized yeast, although this is not necessary. In acclimatizing the yeast, we inoculate a medium containing fermentable sugars and suitable yeast nutrients with yeast and, when fermentation has become active, we introduce an excess of the chosen sulfite and incubate, accompanied, preferably, by stepwise decrements in the pH to the approximate pH at which the yeast will be used. After the completion of the fermentation, the sulfite-yeast cake filtered out forms an inoculum of acclimatized yeast.

The concentration of yeast or acclimatized inoculum in the sulfite-sugar solution is not critical, since a variation in concentration simply varies the rate of fermentation. Inoculum recovered at the end of the process may be used indefinitely to inoculate new batches.

Since yeasts respond best at about 30° C., we prefer this temperature for the fermentation, although it will proceed at any temperature at which the yeasts themselves are active. During fermentation, the activity is increased by continuous or intermittent stirring.

As soon as the sugar-sulfite solution has been inoculated, we adjust the pH of the mixture by the addition of acid or acid forming substance which is substantially non-toxic to yeast in the concentrations used. Such acid may be either organic or inorganic. In the interests of easy separation of the end products, it is desirable to use an acid which will not combine with the positive ion of the sulfite used to form a compound soluble in an alkaline solution. As acidifiers, SO_2 and H_2SO_3 offer additional advantages in that they are cheap, easily removed from the end products, and introduce no new negative ion into the fermentation.

It is desirable to regulate the pH of the fermentation within reasonably close limits to obtain the best results. One purpose of the addition of the acid or acid forming substance, as has been pointed out, is to create a more favorable environment for yeast fermentation. However, the most important reason is to cause the formation of bisulfite ion in the medium in order to fix the acetaldehyde as it is formed. This is necessary to the formation of glycerol. The bisulfite ion is, to some extent, toxic to yeast and it is desirable to regulate its concentration at the highest point consistent with rapid and complete fermentation. Since the bisulfite ion concentration is a function of the pH, control of the latter is a simple and convenient method of regulating the former.

The optimum pH is a function of the sulfite employed and the degree of acclimatization of the yeasts employed, hence it is not possible to give an exact rule for its determination. One skilled in the art can very easily determine the optimum pH by making a test fermentation employing the same constituents as the main process, and varying the pH until the optimum value is found. For example, we have found that a pH in the neighborhood of 4.7 is effective with calcium sulfite, while the limiting pH for magnesium sulfite is about 5.0. The best results are obtained by the use of a pH regulator which automatically and continuously adjusts the pH of the medium by additions of the acidifier.

The fermentation should proceed to completion, which ordinarily takes from 18 to 72 hours, depending on the variables pointed out above. When all of the sugar has been transformed, we remove the precipitate of yeast and excess sulfite by some suitable means, such as filtration or centrifugation. The cake thus obtained is a suitable inoculum for the fermentation of additional batches of sugar. If, however, it is not desired to reuse the yeast, this step may be omitted.

The filtrate, or unfiltered mash, as the case may be, containing the fermentation products and soluble sulfites and bisulfites, is made alkaline by the addition of a slight excess of some alkaline compound. Preferably, although not necessarily, this is the base having the same positive ion as the sulfite used, since this procedure simplifies the process, makes separation and purification of the end products easier, and introduces no new ion into the mixture. When magnesium sulfite is used in the fermentation reaction, magnesium hydroxide may be used to render the solution alkaline. Similarly, when calcium sulfite is used in the fermentation, calcium hydroxide may be used as the alkaline addition compound.

Any suitable method for the isolation and purification of the components of this alkaline mixture may be used. We prefer to remove the ethanol and acetaldehyde by distillation. This also breaks down the acetaldehyde-bisulfite complex and precipitates practically all of the bisulfite as sulfite. Since most of the slightly soluble sulfites are less soluble in hot solution than in cold, it is advantageous to filter out the precipitated sulfite while the solution is still hot. This filtration will also remove the yeast in case it has not already been taken out. The remainder is a solution of glycerol containing small amounts of sulfite which vary with the solubility of the sulfite.

From this solution the glycerol may easily be extracted by vacuum distillation, a selective solvent, or other means. A more economical method, however, is to recycle this glycerol solution by adding to it sugar, inoculum, sulfite, etc. for a repetition of the above described process. We have found that the same solution may be recycled in this way several times without appreciable decrease in the rate of fermentation, and with an appropriate increase in the glycerol concentration for each run. When a high concentration is reached, the glycerol may be recovered by means suggested above or some other suitable procedure.

The following specific examples will illustrate the various steps of the process of our invention:

Example 1

A volume of 1500 ml. of medium was prepared which contained, per liter, 150 g. of dextrose, 3.5 g. of Difco yeast extract, and, as yeast nutrients, 1.5 g. of ammonium chloride, 1.5 g. of $K_3H_3(PO_4)_2$, 0.4 g. of $MgSO_4.7H_2O$ and 0.1 g. of calcium chloride. This medium was inoculated with 195 ml. of a 60-hour culture of stock yeast in a similar medium, and incubated at 30° C. for 12 hours. At that time fermentation was active and 420 g. of $MgSO_3.6H_2O$ were added. The culture was returned to incubation and the pH maintained at 6.5 by a Cameron pH recorder-controller using 50% acetic acid. In 40 hours fermentation had returned almost to normal and in 96 hours was complete. The cake formed by filtering contained magnesium sulfite and thoroughly acclimatized yeast.

Example 2

A volume of 1500 ml. of a medium of the composition described in Example 1 was inoculated with acclimatized inoculum obtained as in Example 1. This was incubated at 30° C. and the pH regulated to 6.2 by a Cameron pH recorder-controller using acetic acid. In less than 72 hours the fermentation was complete. Analysis showed a yield of 23.15% of glycerol on dextrose, or 45.5% of the amount glycerol theoretically obtainable from that amount of dextrose.

Example 3

A volume of 1550 ml. of a medium of the composition described in Example 1 was inoculated with an acclimatized inoculum consisting of calcium sulfite and yeast. This was incubated at 30° C. and the pH regulated at 5.0 by a Cameron pH recorder-controller using sulfurous acid. In less than 72 hours the fermentation was complete. Analysis showed a yield of 21.5% on dextrose, or 42.2% of the amount of glycerol theoretically obtainable from that amount of dextrose.

Example 4

A 200 ml. portion of the resultant of Example 1 was filtered and freed of acetaldehyde and ethanol by distillation. To this was added dextrose to 15% of the solution. This was inoculated with acclimatized inoculum containing magnesium sulfite and yeast and incubated. The pH was not controlled but was about 6.3 to 6.4 during the most active parts of the fermentation. The fermentation was complete in less than 3 days and analysis showed a concentration of glycerol of 5.05 g. per 100 ml. The glycerol content of the original liquor was 2.69 g. per 100 ml., giving an increase of 2.36 g. per 100 ml. as a result of recycling, thus indicating that recycling may be profitably employed.

We claim:

1. In a process for the production of glycerol, the step of fermenting with yeast a fermentable sugar in an acid medium containing a sulfite having a solubility of less than 2 parts in 100 parts of cold water, the sulfite being present in a quantity in excess of the quantity which dissolves in the medium.

2. In a process for the production of glycerol, the step of fermenting with yeast a fermentable sugar in a medium containing a sulfite having a solubility of less than 2 parts in 100 parts of cold water, the sulfite being present in a quantity in excess of the quantity which dissolves in the medium, in which medium the pH is adjusted and maintained at less than 7.0 through the addition of a substance selected from the group consisting of sulfur dioxide and sulfurous acid.

3. In a process for the production of glycerol, the step of fermenting with yeast a fermentable sugar in an acid medium containing calcium sulfite in a quantity in excess of the quantity which dissolves in the medium.

4. In a process for the production of glycerol, the step of fermenting with yeast a fermentable sugar in a medium containing calcium sulfite in a quantity in excess of the quantity which dissolves in the medium, in which medium the pH is adjusted and maintained at less than 7.0 through the addition of a substance selected from the group consisting of sulfur dioxide and sulfurous acid.

5. In a process for the production of glycerol, the step of fermenting with yeast a fermentable sugar in an acid medium containing magnesium sulfite in a quantity in excess of the quantity which dissolves in the medium.

6. In a process for the production of glycerol, the step of fermenting with yeast a fermentable sugar in a medium containing magnesium sulfite in a quantity in excess of the quantity which dissolves in the medium, in which medium the pH is adjusted and maintained at less than 7.0 through the addition of a substance selected from the group consisting of sulfur dioxide and sulfurous acid.

7. In a process for the production of glycerol, the step of acclimatizing yeast by subjecting it to a fermentation in an aqueous medium in the presence of magnesium sulfite in a quantity in excess of the quantity which dissolves in the medium.

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PROCESS FOR THE MANUFACTURE OF GLYCERIN

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11 Claims. (Cl. 195—38)

The present invention relates to the manufacture of glycerin by the fermentation of carbohydrate substances with the aid of yeast and in the presence of magnesium carbonate.

It is the general object of the invention to provide an improved fermentation process for the manufacture of glycerin with the aid of magnesium carbonate wherein the fermentation time is reduced, the yield of glycerin increased, and the yeast rendered recoverable in a form in which it is in condition for re-use in the same process.

Briefly described, the present invention resides in the feature that the controlling action of the magnesium carbonate upon the course of the fermentation is effected and regulated by removing, in any suitable way and during the course of the fermentation, at least part of those reaction products which are more volatile than water, as explained hereinafter.

In carrying out one form of our improved process, a neutral gas is bubbled through the fermenting solution, whereby the solution is agitated and a more efficient abstraction of the volatile components, including carbon dioxide, is insured. As the action of the gas is primarily or entirely the mechanical one of carrying off volatile vapors, any fixed, neutral gas which will not interfere with the fermentation and is nonpoisonous can be used. Thus, nitrogen, oxygen and air may be employed, the last-named being preferred for obvious reasons. The gas is then subjected to a treatment whereby the vapors are recovered for further use. The gas may be passed through one or more scrubbing towers or subjected to any other suitable treatment for the recovery of the abstracted vapors, which consist for the most part of alcohol and aldehyde; and if it is re-circulated through the fermenting mash, it is also scrubbed of its CO_2, both to limit the amount of magnesium carbonate that is dissolved by conversion to bicarbonate and to prevent the pH of the mash from falling below 7, the pH value being kept between 7 and 8 to secure maximum yield of glycerin in a minimum of time.

The production of glycerin by fermentation of carbohydrates with yeast in the presence of magnesium carbonate is itself known. The magnesium carbonate acts as a steering agent which causes the fermentation to deviate from the normal course, in which alcohol is the main product, to a more complex reaction in which a considerable part of the carbohydrate is converted into glycerin. We have found that by continuously removing to a considerable extent the more volatile products, that is, the substances which are more volatile than water, during the course of fermentation as by passing a stream of gas through the fermenting mash in the presence of the magnesium carbonate, and by controlling the pH value of the mash, the fermentation proceeds much more rapidly and gives appreciably higher yields of glycerin.

Preferably the pH during the fermentation is maintained, as already mentioned, at a value of 7 to 8. The amount of magnesium carbonate necessary for this purpose is between 10 and 20 parts for every 100 parts of the fermentable carbohydrate which is present at the beginning of the fermentation.

Where a gas is employed to expel the more volatile products, the stream of gas can be regulated so that about 1 liter per minute is passed through 10 liters of the solution to be fermented. If air is used as the gas, the yeast grows somewhat during the fermentation. In any case, whatever gas is used in the process the yeast is maintained in a healthy state so that it is capable of being utilized again to ferment fresh amounts of carbohydrates according to the present method.

The volatilized materials entrained with the stream of gas can be recovered by passing the gas through scrubbers in which the gas is washed with liquids which absorb the volatilized organic materials like alcohol and acetaldehyde. It is also possible to use adsorbent solid materials like adsorbent carbon, for the recovery of these products.

The fermentation under these conditions, when done in batches, is completed in about 1 day at the temperatures usual for such fermentations, namely, between 30–34° C. Preferably, in addition to the stream of gas, mechanical stirring is used in order to assure favorable contact between the insoluble magnesium carbonate, the yeast, and the solution.

After the fermentation is completed, the insoluble magnesium carbonate and the yeast are easily recovered by filtration. The filter cake containing the magnesium carbonate and the yeast can be utilized directly to ferment new amounts of carbohydrates, a quantity of carbonate being added to make up for losses. Some magnesium is found in the solution and can be precipitated from it in the form of an insoluble magnesium compound, for instance, as carbonate or sulfite. In this way, none of the originally introduced magnesium carbonate is lost and at the same time, the solution is freed from dissolved magnesium ions. The carbohydrate for this purpose can be provided from any of the commercial sources, either sucrose or hydrolyzed starch obtained, for instance, from farm products in known manner.

Example 1

A regular solution is prepared by hydrolyzing wheat according to one of the customary methods. The solution then contains 17% of total reducing sugar. 10 liters of the solution corresponding to 1700 grams of reducing sugars and 170 grams of a pressed yeast containing approximately 72% water, are placed in a fermenting vat equipped with stirrer, gas disperser, and gas outlets, in a constant temperature room of approximately 32° C. Air is passed into this mixture at a rate of approximately 1 liter per minute. The gas outlet is connected with one or more scrubbing towers in which first water and then sodium sulfite is used for washing out alcohol and aldehyde from the gas. The pH during the fermentation is 7 to 7.2, maintained by the addition of 170 grams of $MgCO_3$.

After 26 hours substantially all of the fermentable sugar (1300 grams) has been used up. Filtration yields a filter cake in which approximately 400 grams of yeast on the basis of about 72% water in the yeast are present. Approximately 10% of the fermentable sugars has been utilized for the production of the additional amount of yeast. The filtrate, after concentrating, gives a distillate containing about 310 grams of pure glycerin which amounts to approximately 26% of the sugar used for the fermentation.

Example 2

In a procedure corresponding to that of Example 1, nitrogen was used as the gas with the following results: While the growth of yeast was somewhat less, the yield in glycerin corresponded to 18 grams per 100 grams of sugar subjected to fermentation. After subjecting the nitrogen to scrubbing in order to remove the vapors (or after passing it through a cold condenser to condense the vapors) it is either bubbled through a solution of calcium hydroxide or passed through a scrubbing tower where it meets a spray of calcium hydroxide solution, to remove carbon dioxide and is then re-circulated through the fermenting mash.

The more volatile reaction products of the fermentation may be removed from the fermenting mash in other ways than by being entrained in a current of gas. For example, the fermenting mash may be circulated through a tower into which it is sprayed, whereby the lower alcohols, aldehydes, etc. are vaporized and after being withdrawn from the tower, the vapors may be delivered to a condenser; instead of being passed through a sprayer, the fermenting mash may be passed in thin streams or films over extended flat surfaces, which will encourage vaporization and expulsion of volatile reaction products, including carbon dioxide. The escape of the vapors can be aided by vacuum which may at least in part be produced by the condensation of the vapors in the condenser which is connected with the vaporizing chamber.

We claim:

1. In a process for the manufacture of glycerin by fermentation of carbohydrates with yeast in the presence of magnesium carbonate, the steps which comprise expelling at least part of the more volatile products of the fermentation as they are formed and approximately at the fermentation temperature, and thereafter recovering glycerin from the fermentation liquor.

2. In a process for the manufacture of glycerin by fermentation of carbohydrates with yeast in the presence of magnesium carbonate, the steps which comprise passing a stream of a gas through the fermenting mash to carry off at least part of the more volatile products of the fermentation during the course of fermentation, and thereafter recovering the insoluble matter and the glycerin from the fermentation liquor.

3. Process according to claim 1, wherein about 10 to 20 parts of magnesium carbonate are used for each 100 parts of initial fermentable carbohydrate material.

4. Process according to claim 1, wherein the more volatile products are expelled by subjecting the mash, during the fermentation, to conditions favorable to evaporation.

5. Process according to claim 2, wherein the gas is air.

6. Process according to claim 2, wherein the gas is nitrogen.

7. Process for the manufacture of glycerin by fermentation of carbohydrate material in the presence of magnesium carbonate, which comprises passing a stream of a gas through the fermenting mash during the fermentation to expel volatile substances, and removing the abstracted vapors from such gas.

8. Process according to claim 7, wherein the vapor-free gas is re-circulated through the fermenting mash, after removal of carbon dioxide from such gas.

9. Process for the manufacture of glycerin which comprises subjecting a hydrolyzed wheat solution to the action of yeast in the presence of magnesium carbonate, bubbling air through the fermenting mash during the course of fermentation, scrubbing the vapor-laden gas first with water and then with water containing a soluble sulfite, removing insoluble matter from the fermentation liquor and recovering the glycerin from the liquid.

10. In a process for the manufacture of glycerin by fermentation of carbohydrates with yeast in the presence of magnesium carbonate, the steps which comprise expelling at least part of the more volatile products of the fermentation as they are formed while maintaining the magnesium carbonate during the fermentation in excess of the quantity required for neutralization of the liquor, and thereafter recovering glycerin from the fermentation liquor.

11. Process according to claim 10, wherein the expulsion of the more volatile components is effected by mechanically agitating the fermenting mash and bubbling a neutral gas therethrough.

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UNITED STATES PATENT OFFICE

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FERMENTATIVE GLYCEROL PRODUCTION

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12 Claims. (Cl. 195—38)

This invention relates to the production of glycerol and more particularly to a process for producing glycerol by the fermentation of sugars in an acid medium.

It has been known that when fermentable sugars are acted upon by yeasts, under normal acid conditions, the product includes primarily ethanol and carbon dioxide together with small amounts of glycerol and acetic acid. The quantity of glycerol produced in such a reaction is extremely small and such a process is, of course, entirely unsuitable for the commercial production of glycerol.

Two general methods, however, have been suggested for the production of glycerol by means of the fermentation of sugars. The first method is known as the "sulfite fixation" process. In this process a soluble sulfite is added to the fermentation mixture in sufficient quantity to produce fixation of acetaldehyde which is formed in the fermentation and thus to shift the equilibrium of the reaction to increase the quantity of glycerol which is formed. The other general method is known as the "alkaline fermentation" process wherein the fermentation is carried out in a medium made alkaline by the addition of alkaline salts or bases. Both of these processes are carried out in an alkaline medium which is unfavorable to the growth and action of yeasts and accordingly the yields have not been satisfactory.

Moreover, in both methods it is extremely difficult to separate the glycerol which is produced from the large quantities of soluble salts remaining in the medium after the reaction.

It has also been suggested that glycerol may be obtained in a sulfite fixation process wherein sulphur dioxide is added to the medium in order to fix the acetaldehyde. However, in this latter process the quantities of sulfur dioxide used to obtain satisfactory glycerol formation have been found to be toxic to the yeast.

We have found glycerol may be produced by the fermentation of fermentable sugars in a process in which the difficulties of the prior art have been eliminated and from which satisfactory commercial yields of the glycerol may be obtained. Our methods involve the fixation of the acetaldehyde formed in the fermentation reaction and the consequent shifting of the equilibrium of the reaction to form an increased quantity of glycerol. In our method, reagents are used which can be readily removed after the completion of the fermentation, either by filtration or by volatilization, leaving only relatively small quantities of salts remaining mixed with the glycerol which can then be separated without difficulty. Methods involving the fermentation of fermentable sugars with yeast in acid medium containing slightly soluble sulfites are set forth and claimed in our co-pending U. S. patent application, Serial No. 399,416, filed June 23, 1941, for Glycerol production, now Patent No. 2,388,840, issued November 13, 1945.

The present invention contemplates the fermentation of fermentable sugars with yeast in an acid environment in the presence of ammonium sulfite and ammonium bisulfite or either of these compounds. In the process of this invention, the conversion of the sugar into useful products, including glycerol, is practically complete, and the recovery of each of the products in relatively pure form is readily possible.

In accordance with the present invention a fermentable sugar such as dextrose is mixed with a fermenting organism, such as yeast, yeast nutrients as required and ammonium sulfite and ammonium bisulfite or either of these compounds. Any microorganism normally producing an alcoholic fermentation, the equilibrium of which may be altered to produce glycerol through fixation of acetaldehyde, may be used for the fermentation. For example, certain molds such as some species of genera Fusarium and Mucor can be used. Nevertheless, since the molds are much slower acting than the yeast and are more difficult to handle, yeast is to be preferred. The ingredients are mixed in a slightly acid aqueous medium under controlled conditions of temperature and acidity. As the fermentation proceeds, acetaldehyde and glycerol are produced in direct proportion to each other and ethanol is produced in quantities which are in inverse proportion to the quantities of acetaldehyde and glycerol.

The fermentation reaction is permitted to proceed in the presence of an excess of the ammonium sulfite or ammonium bisulfite until substantially all of the sugar has been fermented, at which time, the yeast may be removed from the medium and the products of the reaction may be separated.

In separating the products of the reaction, the mixture may be treated with a base such as calcium hydroxide to render the mixture alkaline. The mixture may then be subjected to distillation to remove therefrom ammonia, acetaldehyde and ethanol. The base will precipitate the sulfite from the mixture and the precipitate may be separated by filtration or centrifugation. If desired, any calcium remaining in the solution may then be precipitated by the addition of carbon dioxide. Preferably the carbon dioxide is added to a hot solution so as to avoid the formation of soluble calcium bicarbonate. Of course, the addition of the correct chemical equivalent of carbon dioxide will precipitate the calcium as the carbonate rather than as the bicarbonate even in cold solution.

When the mixture has been subjected to distillation and chemical treatment to remove the sulfite therein, the remaining mixture may be distilled to obtain the glycerol in relatively pure form or, if desired, the mixture may be recycled and used as the medium in a new reaction.

The raw material for our process is a fermentable sugar or mixture of such sugars, either in pure form or combined with other substances, as molasses, syrup, etc. For proper action by the yeasts it is necessary that the sugar be in solution. Concentrations of sugar as high as 25 g./100 ml. may be used, although more rapid fermentations will be obtained if the concentration does not exceed 20 g./100 ml. Weak concentrations unduly dilute the end products and make recovery difficult.

To the aqueous sugar solution is added an excess of ammonium sulfite, ammonium bisulfite, or a mixture of ammonium sulfite and ammonium bisulfite or ammonia and sulfur dioxide which combine in the solution to produce ammonium sulfite or ammonium bisulfite. Any desired proportion or mixture of these ingredients may be used. By an excess as the term is used herein is meant a sufficient quantity of the materials so that during the fermentation reaction, free ammonium sulfite or ammonium bisulfite will remain uncombined with the acetaldehyde. It is not necessary to add the entire quantity of sulfite or bisulfite at the beginning of the reaction. In fact, the sulfite and bisulfite are preferably added periodically as the process proceeds.

The excess of ammonium sulfite or ammonium bisulfite, of course, should not be sufficiently great to inhibit fermentation by reason of the toxic effects of the bisulfite ion on the yeast.

The sugar-sulfite mixture is inoculated with yeast. The quantity of yeast inoculum will vary with the conditions of the reaction and with the effect which the sulfite exerts upon the yeast. Since yeast is normally affected by the sulfite and its activity retarded, it is preferable to use in the fermentation reaction an acclimatized yeast.

By an acclimatized yeast is meant a yeast which is produced by inoculating a medium containing sugars and suitable yeast nutrients with yeast and, after fermentation has become active, an excess of ammonium sulfite is introduced into the mixture, being added in small quantities at periodical intervals for a period of several hours. In preparing the acclimatized yeast, the quantities of ammonium sulfite which are added at any one time should not be sufficient to markedly inhibit the fermentation. After the completion of the fermentation the yeast culture so formed is found to be resistant to the inhibiting action of the sulfite and may be used to inoculate a large batch of the fermentation medium in which the sugar fermentation for glycerol production is to be carried out.

The concentration of yeast or acclimatized inoculum in the sulfite-sugar solution may be varied within very broad limits since a variation of the concentration of the yeast will ordinarily only vary the rate of fermentation. The yeast or inoculum which is recovered at the end of the process may be used indefinitely to inoculate new batches of medium. Preferably, the fermentation is carried out at a temperature of approximately 30° C. since yeasts normally respond best at this temperature. However, the fermentation may be carried out at any temperature at which the yeasts are found to be active. During the fermentation reaction, the activity of the yeasts may be increased by continuous or intermittent stirring.

The acidity of the medium should be very carefully regulated in the fermentation reaction since the activity of the yeast and the control of the equilibrium of the reaction by means of which the glycerol is produced in substantial quantities are largely dependent upon the acidity of the medium.

The equilibrium of the reaction is affected by the fixation of the acetaldehyde. This fixation of the acetaldehyde is, in turn, dependent upon the concentration of the bisulfite ion in the medium, since the acetaldehyde forms with the bisulfite ion a complex radical or ion which shifts the equilibrium toward the increased formation of the glycerol and acetaldehyde. In a solution containing sulfite ion and bisulfite ion the concentration of the bisulfite ion is a function of the acidity or pH of the solution in accordance with the well established principles of mass action equilibrium. Accordingly, as the pH of the solution is lowered and the acidity of the solution is increased, the bisulfite ion concentration is increased while, on the other hand, a raising of the pH and a lowering of the acidity produces a decrease in the bisulfite concentration.

The bisulfite ion concentration in the medium should be sufficiently great to provide for the fixation of the acetaldehyde formed and thus produce a shifting of the equilibrium of the fermentation reaction. At the same time, if bisulfite ion is present in substantial quantities it exerts a toxic effect upon the yeast and its concentration, therefore, should not exceed a concentration at which the yeast is substantially unaffected, in a toxic manner, by the bisulfite ion.

The control of the acidity of the solution is important for additional reasons. It has been found that free ammonia is, to a certain extent, toxic to yeast and the maintaining of the medium in an acid condition is, therefore, desirable to avoid the formation and presence of free ammonia. An acid medium is also favorable to the growth of and fermentation by the yeast and is, therefore, to be additionally desired.

The solution should be maintained slightly acid at all times and is preferably maintained in the pH range between 6.0 and 7.0. The optimum pH is a function of the degree of acclimatization of the yeasts employed and hence it is not possible to give an exact rule for its determination.

One skilled in the art can very easily determine the optimum pH by making test fermentations employing the same constituents as the main process and varying the pH until the optimum value is found. For example, we have found that yeast grows satisfactorily at a pH range of between 6.5 and 6.9 in the presence of ammonium sulfite. As the fermentation reaction proceeds the pH of the medium will normally be found to vary somewhat. It is, therefore, desirable to use a pH regulator, for example, a Cameron pH recorder-controller of the conventional type to measure and adjust the pH of the medium continuously as the fermentation reaction proceeds. In regulating the pH of the solution or medium sulfur dioxide or sulfurous acid are preferably used to lower the pH of the solution by increasing the sulfite ion concentration therein. When the pH of the solution is to be raised, ammonia or ammonium hydroxide is preferably used to increase the alkalinity of the solution. When these substances are used to increase or decrease the acidity of the solution, no new ions are introduced into the solution and no additional problems in the separation of the end products of the reaction are created.

The ammonium sulfite is preferably added at periodical intervals since the initial presence of large quantities of ammonium sulfite tends to raise the pH of the medium and since the yeasts develop more rapidly if the medium does not contain excessive amounts of salts. As the fermentation proceeds and the acetaldehyde bisulfite complex is formed, the concentration of the free bisulfite ion in the medium decreases while the pH rises. The periodical addition of the sulfite salt tends to counteract this effect. Nevertheless, the pH should be carefully controlled and adjusted so as to maintain the same substantially constant throughout the fermentation reaction.

The fermentation reaction will ordinarily proceed to completion in between 18 and 72 hours, depending upon the conditions of the reaction. When substantially all of the sugar has been fermented, the precipitate of yeast may, if desired, be removed by any suitable method such as centrifugation or filtration. This yeast may be reused for inoculum for the fermentation of additional batches of sugar.

The fermentation mixture containing the yeast or from which the yeast has been removed, may be made alkaline by the addition of a slight excess of some alkaline substance, such as a hydroxide, oxide or carbonate of a metal of the alkaline earth group. Such a substance will react with the sulfite and precipitate them as insoluble compounds. Preferably, although not necessarily, the base may be calcium hydroxide.

Any suitable method for the isolation and purification of the components of alkaline mixture may be used. Preferably, the mixture is distilled to remove therefrom ammonia, ethanol and acetaldehyde. The distillation destroys the acetaldehyde-bisulfite complex and precipitates substantially all of the bisulfite as calcium sulfite. Since most of the slightly soluble sulfites are less soluble in hot solution than in cold, it is advantageous to filter out the sulfite precipitate while the solution is still hot. This filtration will also remove the yeast from the medium if it has not already been separated. The ammonia from the distillation may be recovered by any suitable or conventional method. The excess of the base such as calcium hydroxide is removed from the solution by introducing into the hot solution, carbon dioxide which will form an insoluble carbonate. The carbonate precipitate may then be removed from the solution by filtration. The remaining filtrate is a solution of glycerol containing very small amounts of soluble salts.

The filtrate containing the glycerol may be subjected to vacuum distillation or to treatment with a selective solvent or to other suitable means for separating the glycerol therefrom. If desired, the glycerol solution may be recycled and used as the medium in a succeeding operation, the sugar, inoculum, ammonium sulfite, etc. being added to the glycerol solution for this purpose. The same solution may be recycled in this manner for several times with an appreciable decrease in the rate of fermentation and with an appropriate increase in the glycerol concentration of the solution after each operation.

A specific example of a process embodying the invention is as follows: A medium is prepared containing, per liter, 150 g. of sugar (as dextrose), ammonium sulfite and/or ammonium bisulfite equivalent to about 60 g. of sulfur dioxide, and any necessary yeast nutrients. The yeast nutrients may suitably be supplied by addition of corn steep liquor and inorganic salts. If a raw material such as molasses, which contains some yeast nutrients, is used as a source of sugar, the additional nutrient requirement, if any, may be determined by experimentation. If pure sugars are used we have found that adequate yeast nutrients are supplied by the addition, per liter, of 2.0 to 4.5 g. of heavy corn steep liquor, 1.5 g. NH_4Cl, 0.75 g. $K_2HPO_4.3H_2O$, 0.75 g. KH_2PO_4, 0.2 g. $MgSO_4.7H_2O$ and 0.1 g. $CaCl_2$. The sulfite may be added as a solid salt or may suitably be prepared as required by the addition of requisite amounts of ammonia (or ammonium hydroxide) and sulphur dioxide (or sulphurous acid). The pH of the medium is adjusted to about 6.5 by addition of ammonium (or ammonium hydroxide) or sulphur dioxide (or sulphurous acid) as required and inoculated with an active yeast culture.

The yeast culture employed may consist of yeast cells filtered or centrifuged from a previous fermentation, or may be prepared as needed in the following manner: A culture of pure yeast is inoculated into a sterile medium containing 150 g. of sugar per liter and necessary yeast nutrients. After the fermentation has become active, portions of ammonium sulfite (as the solid or in concentrated solution) are added at intervals. The length of the intervals between the sulfite additions depends upon the activity of the fermentation. The amount of sulfite added at any one time and the intervals between the additions must be regulated so that active proliferation of the yeast and active fermentation is never interrupted. We have found that the addition of 5 g. portions of ammonium sulfite per liter at intervals of about 6 hours is generally satisfactory. At the end of 48 to 72 hours the acclimatized culture may be used to inoculate a batch of medium, prepared as stated above, for the main glycerol fermentation. A proportion of inoculum of one-tenth the volume of medium is suitable, although a greater or less proportion may be satisfactorily employed.

After inoculation the pH is maintained at the desired acid pH which may be at approximately 6.8 (most suitably by means of a pH recorder-controller such as the Cameron instrument, or other) using sulfur dioxide (or sulfurous acid). During the course of the fermentation the progress is followed by periodic sugar analyses and the fermentation is judged to be complete when no further reduction in sugar content is found. Upon completion of the fermentation, if it is desired to employ the yeast for inoculating a new batch of medium, this is separated by centrifugation or filtration. If the yeast is not to be so used, this step may be omitted.

To the fermented liquid calcium hydroxide in excess of the amount required to make the mixture distinctly alkaline is added, either as solid or as a slurry with water, and the mixture is agitated. The volatile materials are then removed by distillation, and the ammonia, acetaldehyde and ethanol are separated. The solids remaining after the distillation (calcium sulfite and excess calcium hydroxide) are removed by filtration or centrifugation. Calcium in solution is precipitated by adding carbon dioxide to the hot solution, and the resulting calcium carbonate removed by filtration or centrifugation. The glycerol remaining in the solution may then be recovered by suitable means, such as evaporation of the water followed by vacuum distillation or solvent extraction of the glycerol. Or, if it is desired, this solution may be recycled by the addition of more sugar, yeast nutrients, sulfite and yeast inoculum and the fermentation repeated. Such recycling may be practiced one or more times to build up the concentration of glycerol before its recovery, thus rendering the step of recovery more economical.

The control of the acidity of the medium during the fermentation reaction is extremely critical. By maintaining a relatively high pH in the acid medium or, in other words, by maintaining the medium in a slightly acid condition, the presence of excess quantities of bisulfite ions is avoided and the yeast is, therefore, not subjected to the toxic action of large quantities of bisulfite ion. At the same time, the maintaining of the pH below 7.0 eliminates any free ammonia which otherwise might be present in the medium and which is toxic to the yeast at least to a limited extent. The acid medium is also much more favorable to yeast growth and fermentation than is an alkaline medium.

The control of the pH of the medium is, therefore, important in the carrying out of the fermentation reaction.

The maintaining of the medium in an acid condition is also important in the shifting of the equilibrium of the fermentation reaction to obtain relatively large quantities of glycerol. In the absence of such a medium, bisulfite ion may not be formed in sufficient concentration to provide for the fixation of the acetaldehyde.

The bisulfite ion concentration in the medium is a critical factor in the fermentation reaction. At all times during the course of the fermentation reaction, bisulfite ion should be present in sufficient concentration to fix all of the acetaldehyde that is formed. On the other hand, the concentration of the bisulfite should be low enough to avoid any substantial inhibiting of the fermentation reaction by reason of the toxic effect of the bisulfite ion on the yeast or other fermenting organism. The maximum allowable concentration of bisulfite ion will, of course, vary with the degree of acclimatization of the fermenting organism and with the particular organism used.

The bisulfite ion concentration in the medium is affected by numerous factors. The concentration is increased with decreases in the pH of the medium and with increases in the sulfite ion concentration. The concentration of bisulfite ion also varies with the concentration of the acetaldehyde-bisulfite complex in the medium, as well as with the changes of temperature in the medium.

Accordingly, the conditions of the fermentation should be so controlled as to control the bisulfite ion concentration in the medium.

The fermentation may be carried out in a slightly acid medium in the presence of bisulfite ion in a quantity sufficient to fix the acetaldehyde and insufficient to have a toxic effect upon the fermenting organism. The medium is preferably maintained at a pH of between 6.0 and 7.0 and is adjusted to maintain the pH of the medium substantially constant as the fermentation proceeds.

The fermentation reaction may be carried out in the presence of bisulfite ion in a medium wherein the acidity is carefully controlled. Although the bisulfite ion may be obtained from various sources, it is preferably provided by adding ammonium sulfite or ammonium bisulfite to the medium.

Although the process of the invention has been described in relation to particular conditions and ingredients, it will be understood that these have been given for the purpose of illustration. Changes and variations in the process, therefore, and particularly in the quantities and proportions of the ingredients and in the conditions of the reactions may readily be made without departing from the spirit and scope of the invention.

We claim:

1. In a process for the production of glycerol the step of fermenting a fermentable sugar in a slightly acid medium containing a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity sufficient to fix the acetaldehyde formed in the fermentation and insufficient to substantially inhibit the fermentation reaction.

2. In a process for the production of glycerol the step of fermenting a fermentable sugar in a slightly acid medium having a pH of between 6.0 and 7.0 and containing a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity sufficient to fix the acetaldehyde formed in the fermentation and insufficient to substantially inhibit the fermentation reaction.

3. In a process for the production of glycerol the step of fermenting a fermentable sugar in a slightly acid medium containing a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity in excess of that sufficient to fix the acetaldehyde formed in the fermentation.

4. In a process for the production of glycerol the step of fermenting a fermentable sugar with yeast in a slightly acid medium having a pH between 6.0 and 7.0 and containing a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity sufficient to fix the acetaldehyde formed in the fermentation and insufficient to substantially inhibit the fermentation reaction.

5. In a process for the production of glycerol the steps of mixing a fermentable sugar, an acclimatized yeast organism, a yeast nutrient, and a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite in an aqueous medium having a pH in the range between 6.0 and 7.0, said substance being present in a quantity in excess of that sufficient to fix the acetaldehyde formed in the fermentation, and adjusting the pH of the medium to maintain the same in said range while fermentation occurs, the pH being increased by increasing the sulfite ion concentration in the medium and the pH being decreased by increasing the ammonium ion concentration in the medium.

6. In a process for the production of glycerol the steps of fermenting a fermentable sugar with yeast in a slightly acid medium containing a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity in excess

of that sufficient to fix the acetaldehyde formed in the fermentation, periodically adding to the medium a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, and maintaining the pH of the medium substantially constant and the medium slightly acid throughout the fermentation.

7. In a process for the production of glycerol the steps of fermenting a fermentable sugar with yeast in a slightly acid medium having the pH in the range between 6.0 and 7.0 and containing a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity in excess of that sufficient to fix the acetaldehyde formed in the fermentation, periodically adding to the medium a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, and adjusting the pH of the medium to maintain the same in said range while fermentation occurs, the pH being increased by increasing the sulfite ion concentration in the medium and the pH being decreased by increasing the ammonium ion concentration in the medium.

8. In a process for the production of glycerol, the steps of fermenting a fermentable sugar with yeast in a slightly acid aqueous medium containing a substance selected from a group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity sufficient to fix the acetaldehyde formed in the fermentation and insufficient to substantially inhibit the fermentation reaction adding to the fermented medium a cation which combines with the sulfite ion to form a substance of low solubility, and separating said substance from the medium.

9. In a process for the production of glycerol, the steps of fermenting a fermentable sugar with yeast in a slightly acid aqueous medium containing a substance selected from a group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity sufficient to fix the acetaldehyde formed in the fermentation and insufficient to substantially inhibit the fermentation reaction adding to the fermented mixture a base having a cation which combines with the sulfite ion to form a substance of low solubility, subjecting the fermented mixture to distillation, and separating the precipitate from the medium.

10. In a process for the production of glycerol, the steps of fermenting a fermentable sugar with yeast in a slightly acid medium having a pH between 6.5 and 6.9 and containing a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity in excess of that sufficient to fix the acetaldehyde formed in the fermentation, precipitating the sulfite ion by adding to the medium a substance selected from the group consisting of hydroxides, oxides and carbonates of metals of the alkaline earth group,

subjecting the fermented mixture to distillation to remove therefrom ammonia, acetaldehyde and ethanol, separating the precipitate from the medium, and adding carbon dioxide to the medium to precipitate as calcium carbonate any soluble calcium remaining in the medium.

11. In a process for the production of glycerol, the steps of fermenting a fermentable sugar with yeast in a slightly acid aqueous medium having a pH in the range between 6.5 and 6.9 and containing a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite, said substance being present in a quantity sufficient to fix the acetaldehyde formed in the fermentation and insufficient to substantially inhibit the fermentation reaction, adjusting the pH of the medium to maintain the same in said range throughout the fermentation, adding to the mixture a substance selected from the group consisting of hydroxides, oxides and carbonates of metals of the alkaline earth group to precipitate the sulfite ion in the medium, subjecting the fermented mixture to distillation to remove therefrom ammonia, acetaldehyde and ethanol, and separating the precipitate from the medium.

12. In a process for the production of glycerol wherein a fermentable sugar is mixed with a fermenting organism for producing alcoholic fermentation of said sugar, the steps of mixing with the sugar and fermenting organism a substance selected from the group consisting of ammonium sulfite and ammonium bisulfite in a slight acid medium and adjusting the pH of the medium to maintain the same substantially constant and the medium slightly acid while fermentation occurs, said substance being present in a quantity sufficient to fix the acetaldehyde formed in the fermentation and insufficient to substantially inhibit the fermentation reaction.

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Oct. 24, 1944. J. ZENDER 2,361,000

PROCESS FOR MAKING DIALYZING MEMBRANES AND ARTICLE SO PRODUCED

Filed Oct. 6, 1941

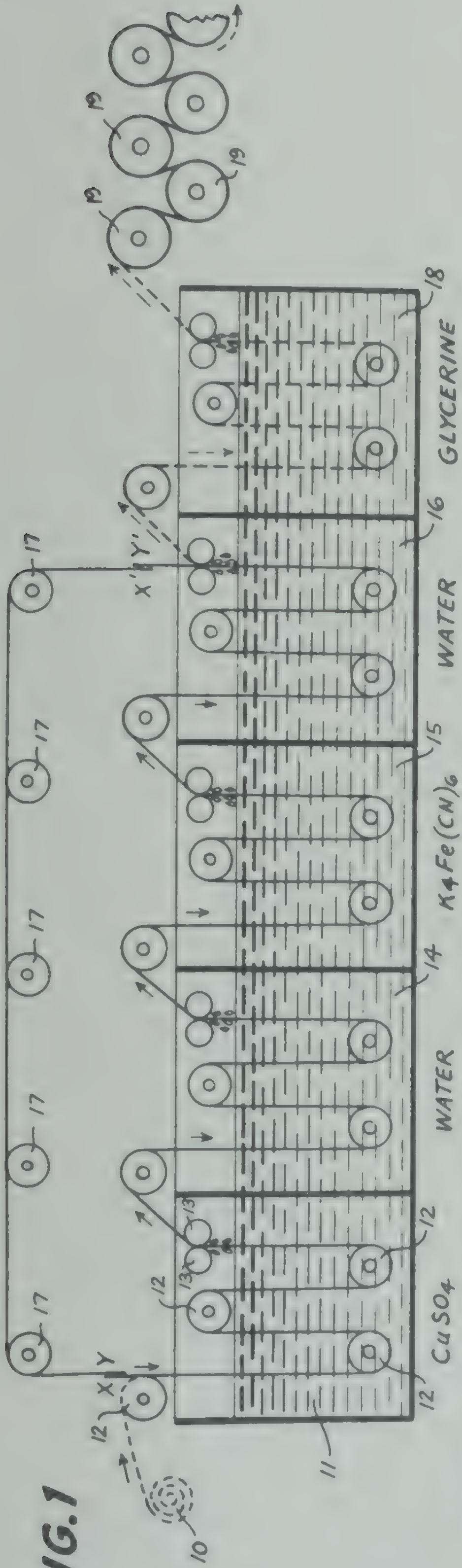

FIG.1

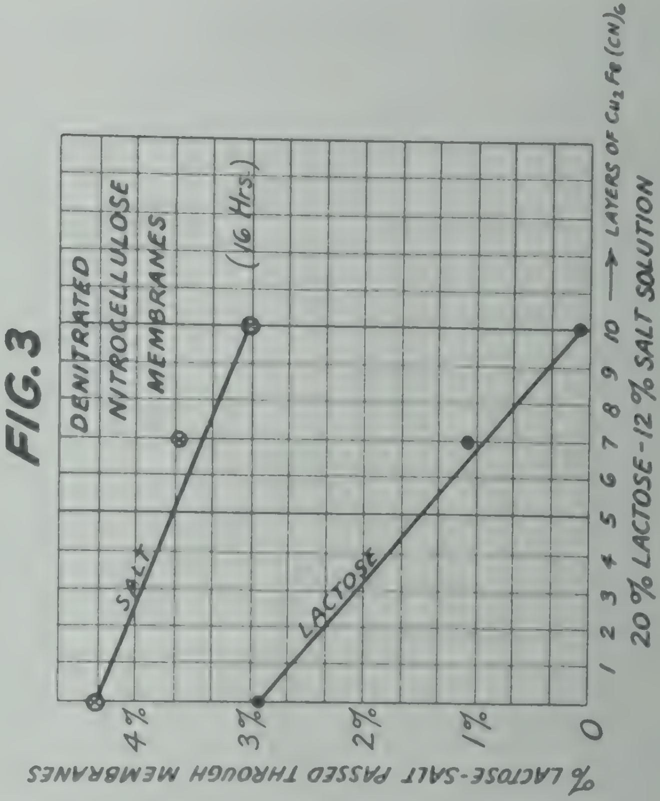

FIG.3

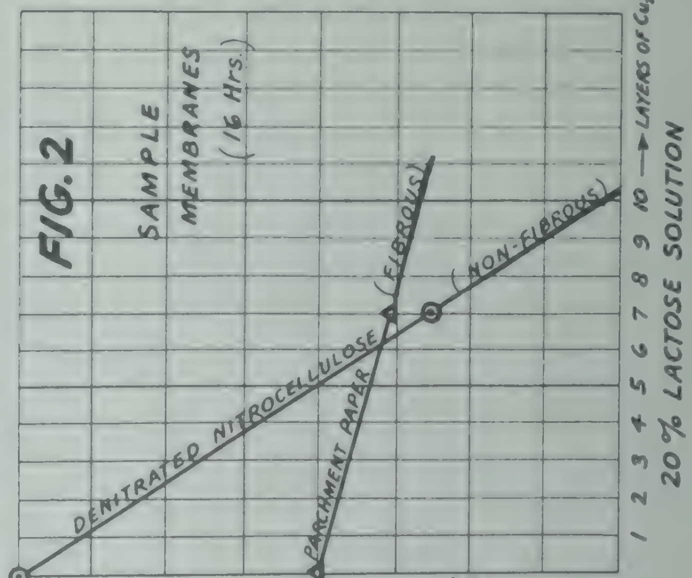

FIG.2

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2,361,000

PROCESS FOR MAKING DIALYZING MEMBRANES AND ARTICLE SO PRODUCED

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Application October 6, 1941, Serial No. 413,804

6 Claims. (Cl. 117—144)

The present invention relates to a method for making dialyzing membranes and to the membranes thus formed, and includes correlated improvements designed to enhance the utility and structure of such membranes.

It has been found desirable to provide a method of separating substances of different molecular sizes from each other or electrolytes from non-electrolytes, by dialysis. For example, it is frequently necessary to be able to separate crystalloids from crystalloids, crystalloids from colloids, and colloids of different molecular sizes from each other when present in the same solution, colloidal dispersion or suspension. To achieve such selective separation of one substance from another efficiently, it has been found necessary to employ a membrane which will permit one of the dissolved substances to migrate through the membrane, while at the same time substantially retaining the other substance.

Attempts have been made to separate mixtures of dissolved substances by dialysis using unglazed porcelain plates impregnated with a single precipitated deposit of copper ferrocyanide. Such membranes have been found to be inefficient and unsatisfactory because the plates are fragile, the speed of dialysis is low and the separation not sharp enough for commercial use. The efficiency of such impregnated plates is low as a substantial amount of the material desired to be retained passes through the membrane and is lost, for the reason that it is difficult to obtain plates uniformly impregnated.

It is a general object of the present invention to provide a method for forming an improved dialyzing membrane which is rapid and efficient in use.

It is a further object of the invention to provide a method for forming a dialyzing membrane which is flexible, tough, and not fragile.

It is a specific object of the invention to provide a dialyzing membrane comprising a pellicle formed of an hydrophilic organic colloidal material having a high selectivity.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

According to the present invention, there is provided a process for forming a semi-permeable membrane for dialyzing comprising treating a hydrophilic organic pellicle, in sequence, with a plurality of water-soluble inorganic compounds which react with each other to form in situ, within the pellicle, a deposit of a water-insoluble inorganic substance, and thereafter repeating said treatments to form a plurality of such deposits within the same pellicle. In its now preferred embodiment the dialyzing membrane of the invention comprises a hydrophilic organic pellicle impregnated with a plurality of gelatinous deposits of an insoluble inorganic substance formed in situ within the pellicle.

The expression "pellicle of hydrophilic organic colloid" as used in the specification and claims is meant to include fibrous and/or non-fibrous film-forming materials which are capable of absorbing water and swelling in water.

The invention accordingly comprises the several steps and relation of one or more of such steps with respect to each of the others, and the article possessing the features, properties, and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention reference should be made to the following detailed description taken in connection with the accompanying drawing, in which:

Fig. 1, diagrammatically illustrates one type of apparatus suitable for carrying out one embodiment of the process of the invention;

Fig. 2 is a graph showing the relative permeability of two different membranes formed according to the invention; and

Fig. 3 is a graph showing the effective separation of salt from a sugar-salt solution employing one type of membrane formed in accordance with the invention.

The pellicles employed in forming the semi-permeable membrane of the invention may be formed of fibrous and/or non-fibrous hydrophilic organic materials as a class.

The non-fibrous materials, from which pellicles may be formed, comprise film-forming water-swelling (i. e. hydrophilic) colloids as a group such, for example, as cellulose hydrate, alkali-soluble cellulose ethers, hydrophilic cellulose esters, hydrophilic mixed ester-ethers of cellulose, gelatin, casein, de-acetylated chitin, water-swelling resins and the like. The hydrophilic cellulose ethers may comprise the alkyl ethers, the hydroxy-alkyl ethers, the carboxy-alkyl ethers, and the mixed ethers such as alkyl hydroxy-alkyl cellulose ethers, and the cellulose ether xanthates. The cellulose esters which may be used include water-swelling compounds such as low-nitrated cellulose nitrate, low esterified cellulose acetate and cellulose formate, and the like. The cellulose hydrate may be regenerated from viscose or from cuprammonium solutions of cellulose, or from solutions of cellulose in inorganic or organic solvents. Among the water-swelling resins which may be used are the water-swelling polymers of acrylic acid, water-swelling urea-formaldehyde resins, water-swelling methyl-methacrylates, phenol-formaldehyde resins in the "A" stage, and the polyvinyl alcohol resins in the "A" stage, and the like.

The hydrophilic fibrous materials from which the membrane may be formed, comprise organic pellicles formed of parchment paper such as "Patapar," pellicles formed of leather scrap such as the product sold as "Brechteen," and the fibre-bonded felted papers made according to the co-pending application of Carleton S. Frances, Ser. No. 300,876, filed October 23, 1939.

In the preferred embodiment there is employed a membrane formed of denitrated nitrocellulose. The pellicle employed in the invention as the dialyzing membrane may be in the form of a foil, film, sheet, bag or tubing.

In the preferred practice, the inorganic reactants used to produce the plurality of inorganic deposits within the pellicle are applied to the membrane in dilute solution in a suitable solvent, preferably one having a swelling action on the particular membrane. Suitable solvents for use with and adapted to swell the pellicles of the class herein used for the membrane comprise water, or substances miscible therewith such, for example, as the lower monohydric aliphatic alcohols such, for example, as ethyl alcohol; the polyhydric aliphatic alcohols such, for example, as glycerine and di- or tri-ethylene glycol; triethanolamine and the like, or mixtures of one or more of these solvents with each other or with water.

In order to prepare such sheet material for impregnation, it is often desirable to swell the sheet material and/or treat it with various substances to remove impurities before passing the sheet into the solution of copper sulfate. Thus, a swelling agent such as zinc chloride, sodium hydroxide, calcium thiocyanate and the like may be used for pre-treating the sheet material prior to impregnation in order to facilitate impregnation and/or depositing the insoluble copper ferrocyanide in situ.

It has also been found desirable to treat the sheet material with a detergent, saponifying agent and the like, such as sodium perborate to remove such impurities as oil film, grease, dirt, etc. prior to impregnation. Thereafter the sheet may be rinsed to remove the sodium perborate, or it may be further treated with an acid such as a dilute solution of acetic acid, oxalic acid, etc. to neutralize the residual perborate. The sheet material may then be washed, whereupon it may then be treated with a swelling agent, or impregnated in the manner described to form the membrane.

In its simplest embodiment, the process requires the use of two reactants which shall be referred to hereinafter as "reactants A and B" which react to form a gelatinous insoluble precipitate within the pellicle, and the solutions thereof will be designated respectively as solutions "A" and "B." In general, insofar as the chemical nature of the reactants A and B is concerned, it is not material in which order the solutions thereof are applied to the material.

In the now preferred procedure it has been found desirable, after treating the material with the first solution, to allow sufficient time for the solvent to diffuse through the surface and carry the reactant into the body of the material. On the other hand, it is desirable to remove the surface liquid resulting from treating the material with the first solution so that the reaction occurs only with the absorbed liquid within the pellicle, and thereafter applying the second liquid. The surplus of the first solution may be removed by the use of doctor blades, squeeze rolls or other suitable means and/or by rinsing the treated pellicle with water, and the second solution B is then applied preferably by the use of a bath. As the second solution B diffuses within the pellicle, the reagents A and B react to form the gelatinous insoluble precipitate within the body of the pellicle. The pellicle is again rinsed or washed to remove any surface deposits of the insoluble compound. Thereafter this sequence of steps is repeated until sufficient deposits of the insoluble compound are formed to attain the objects of the invention.

By way of illustrating the steps of the process of the invention, but not by way of limitation, there may be given the following examples of inorganic reactants and insoluble products thereof which are suitable for use in the process:

Table 1

	Reactant A	Reactant B	Precipitate
1	Copper sulfate	Potassium ferrocyanide.	Copper ferrocyanide.
2	Copper tartrate	Sodium ferrocyanide	Do.
3	Ferric chloride	Potassium ferrocyanide.	Ferric ferrocyanide.
4	Nickel sulfate	do	Nickel ferrocyanide.
5	Calcium chloride	Sodium phosphate	Calcium phosphate.
6	Zinc chloride	Potassium ferrocyanide.	Zinc ferrocyanide.
7	Aluminum sulfate	Sodium hydroxide	Aluminum hydroxide.

According to the preferred process a thin sheet of denitrated nitrocellulose is impregnated with a dilute solution of copper sulfate. The sheet is then gently rinsed with water to remove any surface deposit and passed into a solution of potassium ferrocyanide whereupon an insoluble deposit of copper ferrocyanide is formed in situ within the pellicle. The membrane is then gently rinsed to remove any surface deposit and the process then repeated, passing the sheet from copper bath to ferrocyanide bath, to form a plurality of such layers or deposits of insoluble copper ferrocyanide in situ. From 2 to 15 such complete treatments are performed on the sheet material, forming a like number of consecutive deposits or layers of copper ferrocyanide within the sheet material. The dialyzing membrane thus formed is capable of selectively separating suspended or dissolved particles from other substances in solution, depending upon the nature of the particles and the number of layers of precipitate formed in the pellicle.

For purposes of illustration but not by way of limiting the invention, reference should be had to Fig. 1 of the drawing, wherein denitrated nitrocellulose film 10 is passed over idling rollers 12 in a sinuous manner to thoroughly impregnate the sheet with the copper sulfate solution contained in vessel 11. The film is then passed between squeeze rollers 13 in order to remove excess copper sulfate solution, then through a water bath 14. The traverse of the film through the bath 14 should be regulated to remove copper sulfate from the surface but not substantially from the interior of the pellicle. The sheet is next passed through bath 15 comprising an aqueous solution of potassium ferrocyanide, whereupon copper ferrocyanide is precipitated within the sheet material. The sheet material is then passed through a bath of water **16** to remove excess potassium ferrocyanide and loose deposits of copper ferrocyanide adhering to the surface. The process is then repeated, passing the sheet material over supporting rollers **17**, again through the initial copper sulfate solution in bath **11**, through water bath **14**, then once more into the potassium ferrocyanide bath **15** to precipitate a second layer or deposit of copper ferrocyanide within the sheet material. In order to make the process continuous the sheet material may be joined upon itself at X—Y. Repeating the above process there is formed successively a plurality of deposits of copper ferrocyanide within the sheet material. The process is continuous and may be repeated as often as desired, or until it has been found that a sufficient number of layers or deposits have been formed within the pellicle.

After a sufficient number of deposits have been thus formed, the sheet is broken at X′—Y′ and passed through plasticizing bath **18** containing a plasticizer such as 10–20% glycerine or other suitable plasticizer known to the art, then over drying rollers **19** and the sheet material dried and finished in the usual manner.

Referring to Fig. 2 there is shown the result of dialyzing a 20% aqueous solution of lactose through membranes formed of parchment paper and denitrated nitrocellulose, both types of membranes being formed in accordance with the invention. It will be noted that the untreated parchment paper membrane will permit passage of approximately 2% lactose from solution over a period of 16 hours. After the parchment paper has been treated to form seven deposits of copper ferrocyanide in situ, it will be noted that only 1½% lactose passed through the membrane while after fourteen treatments the amount passed falls to about 1%.

Considering the denitrated nitrocellulose membrane, it will be noted that the untreated sheet will permit passage of approximately 4% of lactose within 16 hours, but after the sheet has been impregnated with seven deposits of copper ferrocyanide, approximately only 1¼% of lactose passes from solution, while after ten deposits substantially no lactose passes through the film. In other words, the untreated denitrated nitrocellulose sheet material will initially pass more lactose from solution than parchment paper but after formation of ten deposits of copper ferrocyanide in situ, the denitrated nitrocellulose sheet is substantially impervious to the lactose, in contrast with the treated parchment paper.

In Fig. 3 there is shown the separation of salt from lactose in an aqueous solution comprising 20% lactose and 12% salt. A sheet of denitrated nitrocellulose having 10 deposits of copper ferrocyanide formed in situ within the sheet material was found to pass substantially none of the lactose from solution during 16 hours, while at the same time 3% of the salt content was extracted and removed from the mixture. Thus, within a reasonable time all of the salt could be removed without substantial loss of any of the lactose.

The dialyzing membranes of the present invention have been found useful in the separation of various mixtures of substances in solution, suspension, colloidal dispersion. The semipermeable membranes can be used for the separation of crystalloids from colloids, for example, the separation of salts and sugars from molasses, milk, blood, latex and the like; separation of colloids of large molecular weights from those of smaller molecular weights, such for example as the separation of mixtures of dextrines having different molecular weights, or the separation of impurities from vitamins, hormones, latex, milk, dextrines and the like.

By way of illustrating various methods of forming the dialyzing membrane of the invention but not by way of limitation thereof, the following examples are given:

Example I

A denitrated nitrocellulose sausage casing having a wall-thickness of 0.0019 to 0.0026 inch was initially treated with a solution of 2% sodium perborate for about 20 minutes to remove oil film and surface deposit. The casing was then washed to remove the excess sodium perborate. The casing was then treated with an aqueous solution comprising from 5% copper sulfate and sufficient ammonium hydroxide to adjust the pH of the solution to from 7.6 to 7.9. Any undissolved copper hydroxide was then filtered off. The casing was treated with this solution from 5 to 25 minutes, gently rinsed to remove any excess solution from the surface and then passed into a bath comprising from 2 to 10% potassium ferrocyanide having the pH adjusted with acetic acid to from 6.0 to 6.5 and allowed to remain in this solution for about 5 minutes. After such treatment the casing was found to have acquired a light brown coloration due to the formation of insoluble copper ferrocyanide within the casing. The process was then repeated nine times, the casing passing from the copper sulfate bath to the potassium ferrocyanide bath, each time forming an additional layer of insoluble copper ferrocyanide in situ and the casing gradually acquiring a browner coloration with each successive deposit thus formed. A casing having 10 layers of copper ferrocyanide formed in situ contains about 25 grams of copper ferrocyanide per square meter of sheet material. Two superimposed membranes were then tested in a dialyzing vessel and found to retain all but 8% of the saccharose present in molasses which comprised 11–12% salt and 65% of sugars, while removing 89% of the salt present in solution.

Example II

A sheet of denitrated nitrocellulose having a wall thickness of 0.0039 inch was treated with a solution comprising approximately 5% Rochelle salt (sodium potassium tartrate) and 5% copper sulphate together with sufficient sodium hydroxide to adjust the pH to approximately 7.5. After treating the sheet with the copper solution for about 15 minutes, the sheet was then gently rinsed with pure water and passed into a solution of potassium ferrocyanide of 10% concentration, containing sufficient quantity of dilute acid to adjust the pH to 6.0–6.5. After 10 minutes a deposit of copper ferrocyanide formed in situ. The sheet material was then washed to remove any surface deposit and the process repeated, passing the film fifteen times through the same baths in the order just described to form a total of 16 successive deposits of copper ferrocyanide in situ. The dialyzing membrane thus formed was found to permit passage of a high percentage of salt from a sugar-salt solution, while retaining substantially all of sugars in solution.

Example III

Parchment paper such as that sold under the trade name "Patapar" was passed into a 3 to 5% ferric chloride solution having the pH adjusted to render the solution slightly acid, i. e., from pH 4–6.9. The sheet was then superficially rinsed to remove surface excess and then passed into a second bath comprising from 2 to 10% potassium ferrocyanide, having the pH adjusted to approximately 7.3 to 8.5, that is, slightly on the alkaline side, whereupon there was formed an insoluble deposit of ferric ferrocyanide in situ. Treatments ranged from 3 to 20 minutes. The sheet was then removed from the potassium ferrocyanide bath, gently rinsed and again treated in the ferric chloride bath and then rinsed again. The above process was then repeated, passing the sheet from ferric chloride bath to potassium ferrocyanide bath, rinsing the sheet between each operation. After twelve such impregnations, the sheet was employed as a dialyzing membrane for selective separation of various substances in solutions of the class described.

Example IV

A sheet of Cellophane was passed through a solution comprising 10% nickel sulfate, 10% Rochelle salt (sodium potassium tartrate) and sufficient sodium hydroxide to adjust the pH to from 7.2 to 9.2. After about twenty minutes the Cellophane was washed to remove surface deposits and passed into a bath comprising from 2 to 10% potassium ferrocyanide having the pH adjusted to 5.2–6.8. The sheet was allowed to stand in this bath for about 10 minutes, again washed to remove surface deposits and the process then repeated, passing the sheet from the nickel sulfate bath to the potassium ferrocyanide bath until the sheet had been impregnated with deposits of nickel ferrocyanide. The sheet was found to be very effective as a dialyzing membrane.

Example V

A sheet of denitrated nitrocellulose having a wall thickness of from 0.0025 to 0.0030 inch was treated with a 2% solution of sodium perborate to cleanse the surface and thereafter rinsed with a dilute solution of oxalic acid to neutralize any remaining perborate. The sheet of denitrated nitrocellulose was then rinsed to remove the sodium perborate or sodium citrate remaining. The sheet was then treated with a 5–10% aqueous solution of zinc chloride having sufficient hydrochloric acid present to adjust the pH to between 4.0 and 6.5. The zinc chloride was allowed to penetrate the sheet material thoroughly for 5 to 15 minutes whereupon the sheet material was sufficiently washed to remove the solution of zinc chloride remaining on the surface, but not to wash out the zinc chloride within the wall structure. The sheet was then passed into an aqueous solution comprising from 5–10% potassium ferrocyanide having the pH adjusted to from 7.5 to 9.8. After about 5 to 10 minutes in contact with the potassium ferrocyanide solution the sheet was removed and found to have become impregnated with a deposit of insoluble zinc ferrocyanide precipitated in situ. The sheet was then washed in water for about a minute to cleanse the surface and the process then repeated, passing the sheet from the zinc chloride solution to the potassium ferrocyanide solution until a plurality of deposits of insoluble zinc ferrocyanide was formed in situ. After about 7 such treatments the sheet material was found to become an effective dialyzing membrane when tested in a dialyzing cell against a molasses solution containing salt. The salt passed through the membrane but the large majority of the sugar was retained in the molasses solution with very little of the sugar passing through the membrane and becoming lost with the salt removed.

It will be noted from the above description and the examples that the pH of the solutions A and B employed in the invention is adjusted to deposit the optimum amount of precipitate in the pellicle in each instance.

The dialyzing membranes may be used in combination with each other, for example, the membranes which may be formed according to the invention may be laminated or placed adjacent one another, or they may be used individually or separately, or in combination with untreated sheets in a dialyzing process.

Among the many advantages which may be mentioned in employing the novel dialyzing membranes herein described, one dissolved substance in a complex solution may be substantially completely separated and removed from said solution with little loss of the other components which are retained in the solution, such for example as a process whereby an electrolyte such as salt dissolved in a complex salt-sugar solution may be separated from the sugars which comprise non-electrolytes, and with minimum loss of sugar from the solution. In employing the membranes in a dialyzing process, the operation proceeds in a uniform and regular manner without necessitating heat and/or pressure, such as would be required in a distillation process. Furthermore, in attempting to separate one or more substances from a complex solution by means of distillation, the quality or chemical nature of such substances is often impaired or destroyed as a result of heating. The dialyzing membrane of the invention has been found to be very effective in efficiently separating various materials dissolved in complex solutions and at the same time such process involves little cost in the way of manufacture, operating expense or labor.

Since certain changes in carrying out the above process, and certain modifications in the article which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described my invention, which I claim as new and desire to secure by Letters Patent is:

1. In a process for forming semi-permeable dialyzing membranes, the steps comprising treating a pellicle of hydrophilic organic colloidal material in sequence, first with a water-soluble inorganic copper salt, thereafter applying a second water-soluble inorganic salt comprising metallic salt of a ferrocyanide, said salts reacting with each other to form a deposit of a water-insoluble inorganic substance within the pellicle, thereafter repeating said treatments to form a plurality of such deposits within the same pellicle.

2. In a process for forming semi-permeable

dialyzing membranes, the steps comprising treating a pellicle of non-fibrous hydrophilic cellulosic material in sequence, first with a water-soluble inorganic copper salt, thereafter applying a second water-soluble inorganic salt comprising metallic salt of a ferrocyanide, said salts reacting with each other to form a deposit of a water-insoluble inorganic substance within the pellicle, thereafter repeating said treatments to form a plurality of such deposits within the same pellicle.

3. In a process for forming semi-permeable dialyzing membrane, the steps comprising treating a pellicle of hydrophilic organic colloidal material in sequence first with a water-soluble inorganic compound and thereafter applying a second water-soluble inorganic compound which reacts with said first compound to form a gelatinous deposit of a water-insoluble inorganic substance within the pellicle, thereafter repeating said treatments to form a plurality of such gelatinous deposits within the same pellicle.

4. As an article of manufacture, a semi-permeable dialyzing membrane comprising a pellicle of hydrophilic organic colloidal material having a plurality of gelatinous deposits of a water-insoluble inorganic substance formed within the pellicle.

5. As an article of manufacture, a semi-permeable dialyzing membrane comprising a pellicle of hydrophilic cellulosic material having a plurality of gelatinous deposits of a water-insoluble inorganic substance formed within the pellicle.

6. As an article of manufacture, a semi-permeable dialyzing membrane comprising a pellicle of hydrophilic regenerated cellulose material having a plurality of gelatinous deposits of a water-insoluble inorganic substance formed within the pellicle.

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UNITED STATES PATENT OFFICE

2,386,381

PROCESS OF PRODUCING A PLASTICIZING COMPOSITION

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No Drawing. Application September 12, 1942, Serial No. 458,139

6 Claims. (Cl. 195—38)

This invention relates in general to plasticizers for pellicles formed of hydrophilic colloids and in particular to a process of making a plasticizing composition for pellicles formed of hydrophilic colloids and to the plasticizing composition so produced. This application is a continuation-in-part of my co-pending application, Serial No. 430,260, filed February 10, 1942.

Heretofore pellicles formed of hydrophilic colloids, such as Cellophane, have been plasticized with glycerol. However, the commercial uses of glycerol are so varied that its market price frequently fluctuates over a wide range. In view thereof, attempts have been made to provide additional sources of glycerol, such as by fermentation of molasses. The production of glycerol by the fermentation of molasses is, however, subject to many drawbacks from a commercial viewpoint, chief of which is the difficulty of separating and recovering the glycerol in a pure form from the products of fermentation. For example a typical black strap molasses contains fermentable sugars 40 to 48%, unfermentable sugars 5 to 8%, organic colloids (proteins, gums, etc.) 19 to 23%, ash 5 to 8%, and the remainder water. To this complex system there are added nutrient salts and compounds necessary to maintain the pH value. After fermentation, the mixture contains all of the unfermentable matter and in addition the products of fermentation. After fermentation, the product includes glycerol, ethyl alcohol, acetic acid, acetaldehyde, and a tract of fusel oil.

It is obvious therefore that the glycerol must be separated from (*a*) the inorganic salts, (*b*) the organic crystalloids including the organic salts and the unfermentable sugars, (*c*) the organic colloids such as the proteins and gums, and (*d*) the volatile organic compounds. The separation of the glycerol in a pure form from all of these classes of substances is a tedious, expensive and complicated process. However, since plasticizers for transparent hydrophilic pellicles must be odorless, and colorless, and leave the pellicle non-tacky, it is not possible to use the glycerol mixture obtained by such prior fermentation of molasses without purification.

It is a general object of the present invention to provide a simple and economical method of making a plasticizing composition for hydrophilic colloids.

It is a more specific object of the invention to provide a method of making a plasticizing composition for hydrophilic pellicles by fermentation in a simple and economical manner.

It is another specific object of the invention to obviate the necessity of expensive and complicated methods of separating glycerol from the products of fermentation, as required when glycerol is produced by fermentation of molasses as heretofore practiced.

It is another object to provide a plasticizing composition for hydrophilic pellicles containing fermentation glycerol.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

According to the present invention, a composition for plasticizing hydrophilic pellicles is prepared by fermentation using as the fermentable material molasses or a sugar solution. In carrying out the process, the sugar in such solutions is fermented in a known manner with yeast, in an alkaline medium, maintaining the desired alkalinity thereof by the addition of an excess of a water-soluble alkaline compound which reacts with the acetic acid produced during the fermentation to form a hygroscopic acetate and, after fermentation, the volatile substances, except glycerol, are distilled off and recovered, if desired, and the composition thus remaining, is concentrated and then dialyzed to obtain an aqueous solution of the glycerol and the hygroscopic acetate, which solution, with or without further concentration, is employed for plasticizing articles formed of hydrophilic colloids.

For the fermentable materials there are used fermentable sugars such, for example, as molasses derived from cane, beet, corn, or by the hydrolysis of starch. There is preferably used a high-grade or partially purified molasses comprising about 75%–80% fermentable sugars, substantially no unfermentable sugars or colloids and ash about 1.5–3%. The molasses is preferably fermented in the form of a dilute solution containing, for example, from 15 to 20% by weight of sugar. To the dilute molasses or sugar solution suitable nutrient salts may be added to promote the growth and acivity of the yeast. By way of example, there may be used such nutrient salts as ammonium chloride, ammonium sulfate, ammonium phosphate, magnesium phosphate, and the like. For the fermentation of the sugar solution, there may be employed any suitable yeast, such, for example, as the yeast *S. ellipsoideus* (variety Steinberg) as shown in U. S. Patent No. 1,288,398, or the yeast No. 16 as disclosed in the McDermott U. S. Patent No. 1,551,997, or any other suitable culture. The yeast is preferably acclimated to the growth in the sugar by starting the yeast growth in a very dilute sugar solution and then transferring the culture to more concentrated solutions of the sugar until the yeast shows an active metabolism in an aqueous solution of from 15 to 20% by weight of sugar.

During the process of fermentation the pH of the solution is maintained preferably between 7 and 8.5 by the addition of a water-soluble compound giving an alkaline reaction in aqueous solution. Although water-soluble alkaline compounds as a class may be used to maintain the pH, there is employed in the now preferred embodiment an alkaline compound which by reaction with the acetic acid produced during the fermentation will produce a water-soluble acetate having hygroscopic properties. The alkaline compounds used are those which are non-toxic to the yeast. Alkaline compounds for this purpose comprise as a class the water-soluble inorganic alkaline compounds which give an alkaline reaction in aqueous solution, such, for example, as potassium carbonate, potassium hydroxide, sodium carbonate, ammonium carbonate, ammonium hydroxide, and the water-soluble organic bases as a class, such, for example as quaternary ammonium bases, alkyl amines and hydroxyalkyl amines and the like, all of which compounds are characterized by being water-soluble, alkaline in reaction, and by reacting with acetic acid to form hygroscopic acetates. Preferably the acetates produced should be deliquescent salts such, for example, as potassium acetate, ammonium acetate, the ethanolamine acetates and the like, since such salts give better results in softening hydrophilic pellicles.

It has been found that such acetates, in particular, potassium acetate, form excellent plasticizers for pellicles formed of hydrophilic colloids so that the presence of these acetates in the fermentation product is functionally important and, in accordance with the present invention, they are not removed from the products of fermentation.

Therefore, in the now preferred practice there is added to the molasses solution potassium carbonate (alone or in admixture with potassium actate) in an amount sufficient to neutralize the acetic acid formed during fermentation. Preferably, the alkaline compound is used in excess because this appears to increase the production of glycerol. After fermentation the excess may be neutralized with acetic acid. In the presence of the excess of the alkaline compound, the pH rapidly drops during fermentation to about 7.4 and remains at that value.

In the now-preferred embodiment of the composition the ratio of hygroscopic acetate compound to the glycerol should be within the range from 1:2 to 1:3. If the amount of acetic acid produced during fermentation is not sufficient to bring the ratio within the range indicated, the invention contemplates that a suitable quantity of a hygroscopic acetate may be added to the product of fermentation.

The fermentation of the sugar solution may be carried out at any suitable temperature at which the yeast cells show sufficient activity, but in the now preferred embodiment the process is carried out at a temperature of from 30 to 40° C.

After the fermentation process has been completed the fermented product will contain glycerol, ethyl alcohol, the water-soluble acetate, a trace of acetaldehyde, a trace of fusel oil, and a trace of the nutrient salts and unfermented sugar. When a 20% sugar solution has been fermented, the liquid before distillation of the alcohol comprises, for example, glycerol from 4% to 6%, water-soluble acetate from 1% to 2%, and a trace of unfermented sugar and nutrient salts, and the remainder is water. The fermented solution is preferably rendered acid, for example, by adding acetic acid until the pH lies between 5.5 and 6.5 and the alcohol is then distilled off and recovered in a known manner. An acid condition of the solution during distillation is desirable to avoid the production of ammonia and because the stills used are normally made of copper.

This "plasticizing composition" thus produced may then be used for plasticizing articles formed of hydrophilic colloids. However, as the solution thus produced is dilute, the liquid, freed from alcohol, is preferably concentrated to about one-half its volume and fresh molasses added thereto to give a sugar content of about 20% and this mixture is refermented. For refermentation additional potassium carbonate is added if necessary to neutralize the acetic acid produced in the second fermentation and to render the solution slightly alkaline. After the second fermentation, the solution is again rendered acid as above described and the alcohol again distilled off and the solution again concentrated to about 50% of its initial volume. During such distillation, the yeast is killed by the heat. When the final solution is to be dialyzed before use, the presence of the yeast is not objectionable since it does not pass through the dialyzing membrane. When dialysis is not to be employed, the yeast is preferably separated from the glycerol solution by suitable means, such as by filtration. The resulting solution contains, as the essential plasticizers, glycerol and potassium acetate, but it also contains certain colloids and inorganic impurities. Further, when derived from cane molasses, the solution has a black color.

The concentrated solution may be purified and decolorized by suitable chemical or physical treatment. For example, the solution may be separated from the yeast and other colloids by dialysis for which one may use a parchment paper or a non-fibrous membrane such, for example, as regenerated cellulose, with water running counter current to the fermented liquor on the opposite side of the membrane. These membranes may be used in the form of tubes or sheets. The glycerol and potassium acetate, with other water-soluble salts, pass through the membrane into the water. If dialysis is not desired, chemical methods of removing the undesired constituents may be resorted to. For example, iron may be removed from the solution by treatment with oxalic acid. Further, the solution may be clarified by precipitating aluminum hydroxide in situ, which precipitate is allowed to settle and the liquid decanted and/or filtered. The precipitate of aluminum hydroxide tends to remove a substantial amount of the color and various insoluble ingredients. Alternatively, albumin and the tannin may be added to the solution and precipitated with formaldehyde to carry down a substantial amount of the impurities and coloring matter.

When the original solution employed or the solution produced has an objectionable color, the original sugar solution or the fermented liquor may be decolorized by suitable means, such for example as by passing it through activated carbon, silica gel or Activated Alumina. However, when the solution contains colloidal coloring matter which is difficult to remove by such absorbents, the solution is preferably dialyzed first to remove such objectionable coloring matter and then decolorized by such absorbents.

It is to be understood that to the plasticizing composition of the present invention there may be added known plasticizers for hydrophilic colloids, such for example as additional glycerol, a glycol, ethylene glycol, diethylene glycol, an alkylol amine, or its water-soluble salt, sorbitol, urea, and the like.

The plasticizing composition thus produced is adapted for plasticizing hydrophilic colloids as a class in the form of pellicles, filaments, tubes, bands and capsules. For example, the composition may be used to plasticize regenerated cellulose, gelatine, casein, hydrophilic cellulose ethers as a class, such for example as alkyl cellulose ethers, hydroxyalkyl cellulose ethers, carboxy-alkyl cellulose ethers, mixed cellulose ethers, water-swelling cellulose esters as a class, water-swelling synthetic resins as a class, leather, glassine, paper, and the like.

The plasticizing composition produced according to this invention is particularly adapted for use in softening and plasticizing regenerated cellulose pellicles in the production of Cellophane. The regenerated cellulose sheet in the wet gel state is passed through a bath containing the plasticizing composition, the concentration of the composition being so adjusted that the mixture of glycerol and water-soluble acetate comprises from 3.5 to 5% by weight of the bath at 40° C. Such a bath is suitable for making Cellophane of #300 weight. For plasticizing heavier Cellophane, the concentration is adjusted in accordance with the known practice in the art.

By way of illustrating but not by way of limiting the invention, there will be given the following detailed example:

An aqueous solution of cane molasses containing 20% by weight of fermentable sugar, is adjusted to a pH of between 7 and 8 by the addition of from 4% to 5% potassium carbonate. A nutrient solution containing a mixture of calcium hydrogen phosphate, ammonium dihydrogen phosphate or urea and concentrated yeast extract is added. To this solution there is added a suitable yeast culture and the solution fermented at a temperature of 35° C. During fermentation the potassium carbonate neutralizes the acetic acid produced, but the excess carbonate maintains the pH at about 7.4. After fermentation, the pH of the solution is adjusted to a value of 5.5 to 6.5 by the addition of acetic acid. The solution is then distilled and the alcohol recovered. The resulting solution is then concentrated to one-half its initial volume, and fresh molasses is added to give a solution containing about 20% sugar and the fermentation repeated with additional yeast under the initial conditions. After the second fermentation, the solution is again acidified with acetic acid and the alcohol again distilled off and recovered. These operations are repeated until the desired concentration of glycerol has been obtained in the solution. When fermentation is apparently completed, the yeast may be separated from the liquid by filtration. The final solution is dialyzed through a membrane of regenerated cellulose and the glycerol content adjusted to from 3.5 to 5% by weight, whereupon the solution will contain also from 1 to 2.5% potassium acetate. This composition may be used at 40° C. for plasticizing regenerated cellulose in the wet gel state of the weight required for making #300 Cellophane.

It is to be understood that the volatile substances need not be separated from the fermented liquor and such substances may remain in the solution when it is employed for plasticizing the hydrophilic colloid.

While the invention has particular application to the production of plasticizing compositions for hydrophilic colloids, the composition has many other uses and, if desired, the glycerol may be separated from the composition by distillation and utilized for many purposes.

In the appended claims, the expression "sugar solution" is intended to include molasses solutions per se as well as solutions of sugar derived from the partial refining of crude molasses and solutions obtained by the dialysis of molasses, as a result of which operations the organic colloids, such as the proteins, gums, etc., are separated from the sugar solution.

While a process and composition for plasticizing a hydrophilic colloid and the plasticized product so produced are disclosed in this application, no claims are made to such subject matter herein since that subject matter is claimed in my co-pending application, Serial No. 430,260, filed February 10, 1942.

Since certain changes in carrying out the above process and certain modifications in the composition which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A process of producing a plasticizing composition comprising fermenting a fermentable sugar solution to glycerol and acetic acid by means of yeast, maintaining the solution alkaline by the addition of a water-soluble alkaline compound which is adapted to react with the acetic acid to form a hygroscopic acetate, and separating the glycerol and said acetate from the fermented liquor by dialysis.

2. A process of producing a plasticizing composition comprising adding yeast to an aqueous alkaline solution comprising a fermentable sugar, fermenting the sugar solution to glycerol whereupon some alcohol and acetic acid are simultaneously produced, maintaining the solution alkaline by the addition of a water-soluble alkaline compound which is adapted to react with the acetic acid to form a hygroscopic acetate, distilling off the alcohol from said liquor and separating the glycerol and said acetate from the fermented liquor by dialysis.

3. A process of producing a plasticizing composition comprising fermenting molasses containing a fermentable sugar to glycerol and acetic acid with yeast, maintaining the molasses solution alkaline by the addition of a water-soluble alkaline compound which is adapted to react with the acetic acid resulting from the fermentation to form a hygroscopic acetate, rendering the solution acid after fermentation, distilling volatile substances from the fermented liquor without distilling the glycerol therefrom, and dialyzing said fermented liquor to obtain a solution of the glycerol and said acetate.

4. A process of producing a plasticizing composition comprising fermenting a fermentable sugar solution to glycerol and acetic acid with yeast while maintaining the liquid alkaline by

the addition of an alkaline potassium compound which is adapted to react with the acetic acid resulting from the fermentation to form a hygroscopic acetate, distilling volatile substances from the fermented liquor without distilling glycerol therefrom, and dialyzing said fermented liquor to obtain a solution of the glycerol and said acetate.

5. A process of producing a plasticizing composition comprising preparing an aqueous solution comprising a fermentable sugar, yeast and nutrient salts for said yeast, fermenting said solution while alkaline to give alcohol, acetic acid and glycerol, maintaining the liquid alkaline during fermentation by adding a water-soluble alkaline compound which, by reaction with the acetic acid produced, will give a hygroscopic acetate having hygroscopic properties, distilling the yeast and the alcohol from the fermented liquor, concentrating the residue, repeating the fermentation, distillation and concentration until the desired glycerol content is obtained and dialyzing the fermented liquor to obtain an aqueous solution comprising glycerol and said acetate.

6. A process of producing a plasticizing composition comprising fermenting an aqueous alkaline solution comprising a fermentable sugar, yeast and nutrient salts for said yeast to give alcohol, acetic acid and glycerol, maintaining the solution alkaline during fermentation by carrying out the fermentation in the presence of an excess of a water-soluble alkaline compound which, by reaction with the acetic acid produced, will give a water-soluble acetate having hygroscopic properties, distilling the alcohol from the fermented liquor, concentrating the residue, repeating the fermentation, distillation and concentration until the desired glycerol content is obtained, and dialyzing the fermented liquor to obtain an aqueous solution containing glycerol and said acetate.

RALPH T. K. CORNWELL.

Nov. 19, 1946. J. ZENDER 2,411,238

PROCESS AND APPARATUS FOR DIALYZING SOLUTIONS

Filed July 8, 1943 2 Sheets-Sheet 1

FIG. 1.

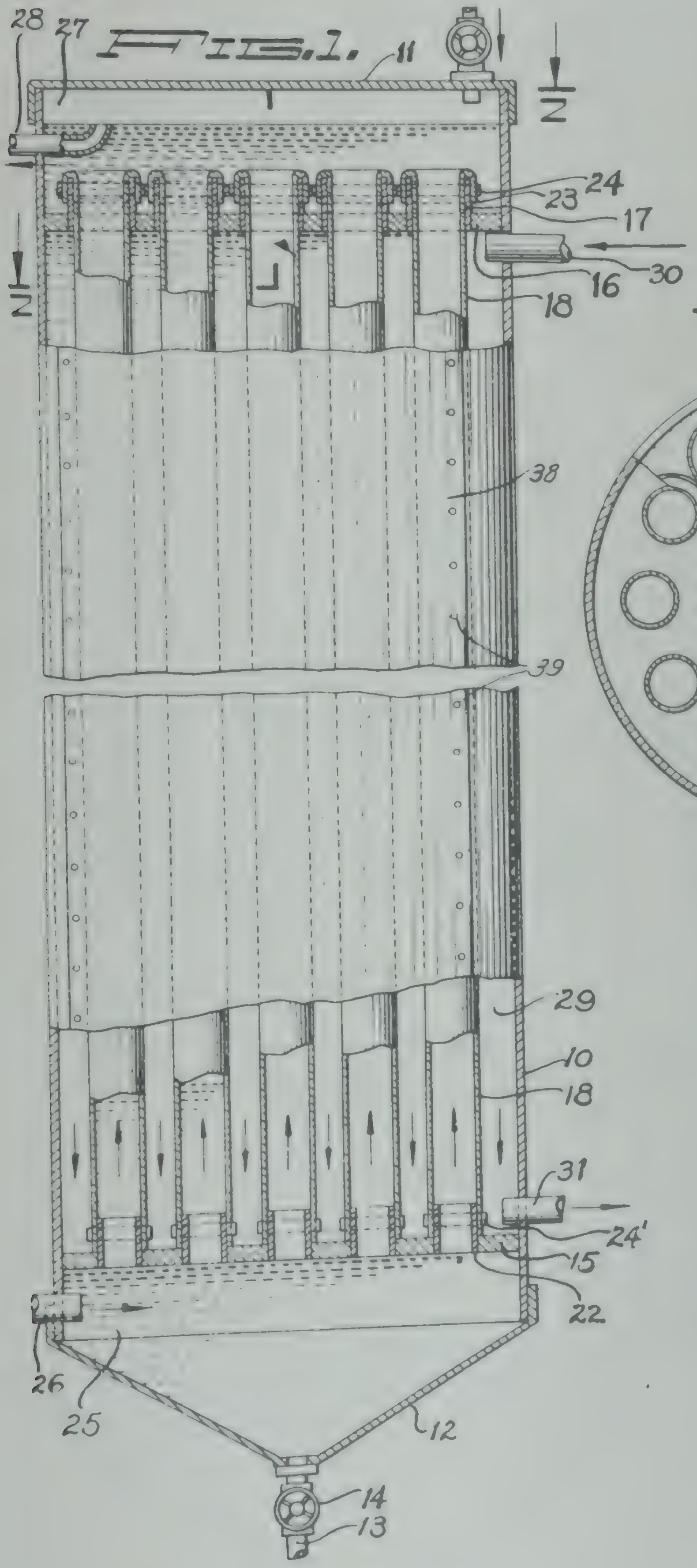
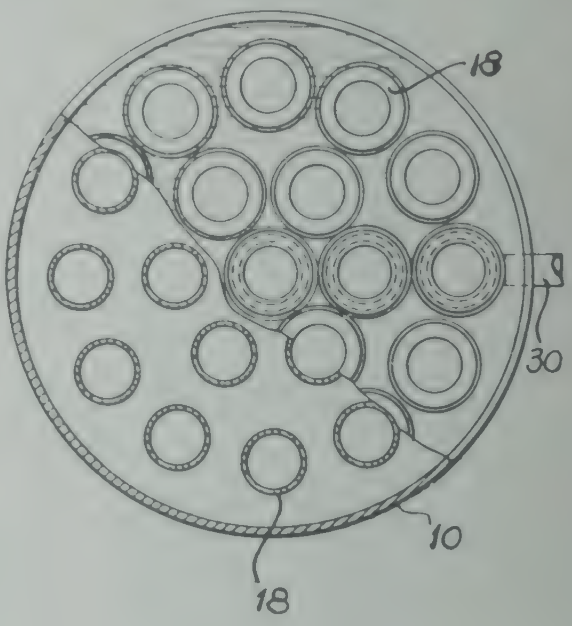


FIG. 2.



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2,411,238

PROCESS AND APPARATUS FOR DIALYZING SOLUTIONS

Filed July 8, 1943

2 Sheets-Sheet 2

FIG. 4.

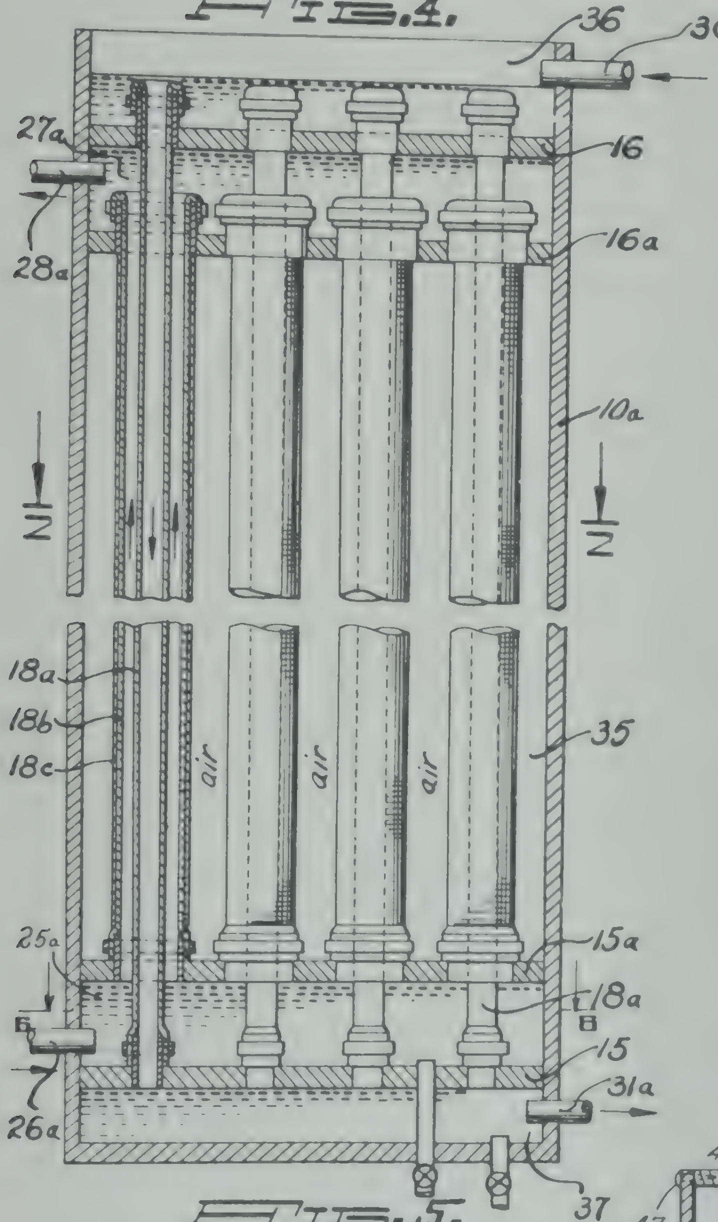


FIG. 3.

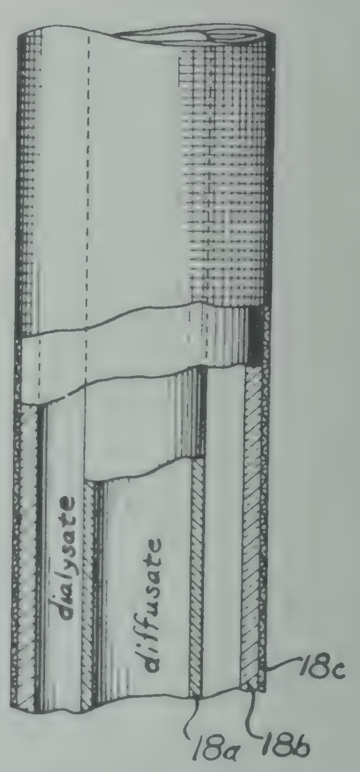


FIG. 5.

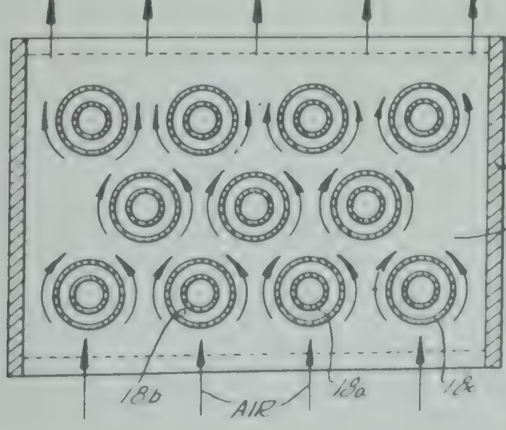
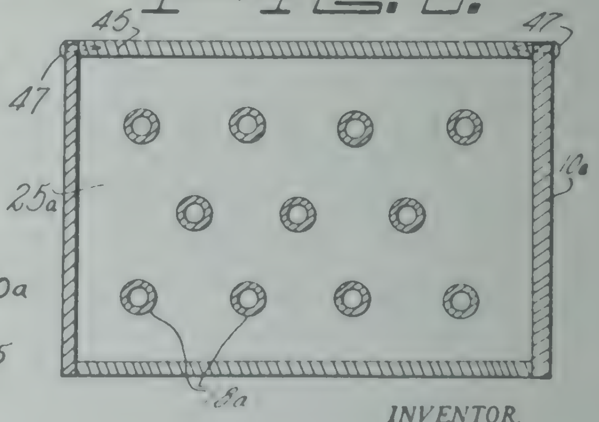


FIG. 6.



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UNITED STATES PATENT OFFICE

2,411,238

PROCESS AND APPARATUS FOR DIALYZING SOLUTIONS

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Application July 8, 1943, Serial No. 493,918

7 Claims. (Cl. 210—8.5)

1

The invention relates in general to dialysis, and, in particular, to a process and apparatus for the separation of a soluble substance from its solution by dialysis, and to correlated improvements designed to enhance the structure and function and to extend the uses of such apparatus.

It has been proposed to dialyze soluble materials from their aqueous solutions through hydrophilic membranes, such, for example, as sheets of regenerated cellulose, parchment paper, and the like. However, dialyzers employing membranes in the form of flat sheets have certain inherent disadvantages. For example, the edges of the sheets must be maintained under pressure or firmly sealed to avoid loss of liquid during dialysis. To clean the apparatus or to replace a broken sheet, it is generally necessary to completely dismantle the dialyzer. Further, to decrease breakage, the membranes must be supported over their surfaces. Finally, such prior apparatus did not provide any means for retarding the dilution of the solution being dialyzed. Thus, sheet dialyzers of prior design have generally been complicated in construction, difficult to repair or to clean and capable of handling only small volumes of liquid.

Accordingly, it is a general object of the present invention to provide a dialyzer which will be capable of handling large volumes of liquid and which will operate rapidly.

It is a further general object to provide a dialyzing apparatus which is easy to construct and to clean and in which broken membranes may be replaced without completely dismantling the dialyzer.

It is another object of the invention to provide a process for the separation of water-soluble substances from their aqueous solutions in a rapid and efficient manner, and in particular for the separation of products of fermentation from the fermented liquor.

A specific object is to provide an apparatus having means for retarding the dilution of the solution being dialyzed.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

According to the present invention, there is provided an apparatus for the dialysis of solutions comprising, in combination, a chamber, a multiplicity of tubular dialyzing membranes disposed therein, means to pass the solution to be dialyzed into contact with one surface of the tube, means to pass another liquid into contact with the other surface of the tube, and preferably means to continuously concentrate the solution being dialyzed so as to increase the rate of dialysis.

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In the now preferred embodiment the apparatus comprises a chamber having headers disposed transversely adjacent each end to divide the chamber into three separate compartments, tubular dialyzing membranes connected at each end to the headers and communicating with a common liquid compartment, and means for passing a fluid around the tubes in the central compartment.

In the following specifications and in the appended claims, the term "dialyzate" will be used to designate the solution being dialyzed in accordance with recent usage in the art; the term "diffusate" will designate the solution of the material which diffuses through the membrane during dialysis, and the term "dialysis" will be used to designate the diffusion of soluble substances through a semi-permeable membrane from one liquid into another.

The invention accordingly comprises the features of construction, combinations of elements, and arrangement of parts which will be exemplified in the construction hereinafter set forth and the scope of the invention will be indicated in the claims.

For a more complete understanding of the nature and objects of the invention, reference should be had to the accompanying drawings in which

Fig. 1 represents a side elevation, partly in section, of one embodiment of the apparatus of the invention;

Fig. 2 represents a cross-sectional view of the dialysis chamber of the apparatus of Fig. 1 taken along the line 2—2 thereof;

Fig. 3 is a side elevation, partly in section, of one of the dialyzing tubes used in a second embodiment of the apparatus;

Fig. 4 is a side elevation, partly in section, of the dialyzer of the invention utilizing a double tube;

Fig. 5 is a top plan view, in section, of the apparatus of Fig. 4 taken along the line 5—5 thereof; and

Figure 6 is a top plan view in section of the apparatus of Figure 4 taken along the line 6—6 thereof.

In that embodiment of the apparatus shown in Figs. 1 and 2, the dialyzing chamber proper comprises a vertical outer chamber 10, which is shown as a cylindrical chamber, but which may be of any cross-sectional shape. The chamber is closed at the top by a removable plate 11, and is closed at the bottom by a conical base 12, which is provided with a drain 13 having a valve 14.

Situated adjacent the ends inside the chamber **10**, there are positioned headers **15** and **16**, each provided with a plurality of holes. Short sections of pipe **17** are threaded into the upper header **15** and similar sections of pipe **22** are threaded into the lower header **16**. These pipes serve to anchor the dialysis tubes **18** to the headers.

The chamber **10** is provided with a removable side portion **38** which makes the interior accessible from the outside. When it is desired to change or replace a tube, the apparatus is drained, the bolts **39** removed, and the side portion **38** of the chamber and the plate **11** taken out. The upper end of the tube is then pulled through the section of pipe **17**, and the end turned down over the upper end of the pipe **17** to form the cuff **23**. The band **24**, which may be formed of rubber, as shown, or of metal or the like, is then slipped over the cuff **23**, anchoring it securely to the pipe **17**. A band **24'** similar to the band **24** is then slipped over the free lower end of the tube **18**, and the end of the tube inserted over the upper end of the lower pipe **22**. The band **24'** is then slipped down over the end of the tube **18**, anchoring it securely to the pipe **22**. The coupling shown in Fig. 1 has the advantage of maintaining the maximum diameter of the tube **18** at the joint, and thus does not interfere with the flow of the liquid through the tube **18**.

The dialysis tubes **18** may be disposed and arranged within the chamber **10** in any desired manner, in rows, for example, or in concentric circles as shown in Fig. 2. The space between the tubes can be varied as desired, but in general a distance of the order of ½ to 1 inch is sufficient. It is to be understood that a space exists around all of the tubes illustrated in Fig. 2, and that none of these tubes are in direct contact with each other along their longitudinal surfaces.

It is to be understood that the apparatus shown in Fig. 1 may be constructed and arranged so that the dialyzate may be caused to pass inside the tubes or outside the tubes, but for the purpose of illustration only, the apparatus of Fig. 1 is constructed and arranged so that the dialyzate can be introduced into the lower section **25** of the chamber **10** by means of the pipe **26**, the dialyzate filling the lower section of the pipe upward through the interior of the tubes **18** and filling the upper section **27** until it overflows through the outlet **28**. The diffusate will be introduced into the intermediate chamber **29** at the top through the pipe **30** and will be removed at the bottom through the pipe **31**. It is to be understood that the circulation of the dialyzate and/or of the diffusate may be continuous or intermittent. When it is desired to clean the apparatus, the dialyzate may be drained off through the exhaust pipe **13** which is positioned at the lowermost point of the bottom section **25**.

It should be noted that the present apparatus is so constructed that the dialyzing tubes **18** are completely submerged in liquid so that no portion is in contact with the air. This is a desirable feature since it has been found that certain membranes, particularly those formed of non-fibrous cellulosic materials, are attacked by certain bacteria or organisms found in fermented sugar solutions and molasses resulting in the rapid deterioration of the membrane. This action is avoided or substantially retarded when the membranes are completely submerged in the liquid, and precautions are taken to avoid introducing bubbles of air in either of the liquids. It is also to be understood that the apparatus of the invention can be arranged without transcending the scope of the invention so as to provide that the dialyzate and the diffusate both flow upward or downward in the same direction instead of flowing countercurrent to each other as shown in Fig. 1.

Further, the apparatus of the type shown in Fig. 1 may be so readily modified by anyone skilled in the art, without transcending the scope of the present invention so that the chamber **10** and the tubes **18** are disposed in a horizontal plane. Inasmuch as the tubes **18** during operation are not only completely filled with liquid but also are completely surrounded by liquid, the tubes will require little or no horizontal support. If the tubes **18** are filled with dialyzate, which has a higher specific gravity than the diffusate, the tubes will tend to float so that they can be kept in position merely by suitable guide pins.

There is also shown in Figs. 3, 4, 5 and 6 another embodiment of the apparatus of the invention in which the dialyzing tubes are double or multiwalled. Referring to Fig. 3, this embodiment comprises an inner dialyzing tube **18*a*** surrounded by a dialyzing tube **18*b*** of larger diameter, and, if necessary, supported externally by means of a textile tube **18*c*** made of an open mesh fabric whether of woven, knitted, or braided construction. The surrounding outer dialyzing tube **18*b*** is particularly advantageous when it is desired to concentrate the dialyzate while it is being subjected simultaneously to dialysis. Thus a plurality of the tubes illustrated in Fig. 3 may be supported between the headers as shown in the apparatus of Fig. 4, leaving an air space **35** between the tubes. The side walls of the chamber **35** are solid as shown in the figure. However, there are no front and back walls to the chamber **35**, as is fully brought out in Figure 5. Thus it is possible to blow air through the chamber **35** across the outer surface of the tube **18*c***, thus causing an evaporation of liquid through the wall of the tube **18*b***, as shown in Figure 5.

Positioning the double tubes in the chamber **10*a*** requires the use of double headers at the top and bottom of the chamber. Accordingly, the outer tubes **18*b*** and **18*c*** are affixed to the inner headers **15*a*** and **16*a***, while the inner tube **18*a*** is affixed to the lowermost header **15** and the uppermost header **16**. In this embodiment, it is preferable to have the dialyzate occupy the space between the tubes **18*a*** and **18*b***, and to have the diffusate occupy the space in the interior of the tube **18*a***. Accordingly, referring to Fig. 4, the dialyzate is introduced into the lower section **25*a*** through the inlet tube **26*a*** so that it fills the lower section and rises through the space between the tubes **18*a*** and **18*b*** and fills the upper section **27*a*** and flows out through the exit tube **28*a***. The diffusate can be introduced at the top of the chamber into the section **36** through the pipe **30*a***, whereupon it fills this section and flows down through the interior of the tube **18*a*** and fills the lower section **37** from which it passes through the exit tube **31*a***.

Since the front and back walls of the chamber **35** are open, it is a simple matter to affix the tubes **18*b*** and **18*c*** to the header **15*a***. In order to provide access to the inner tubes **18*a*** in the chamber **25*a*** and to the upper parts of the outer tubes **18*b*** and **18*c*** in the chamber **27*a*** and the upper part of the inner tubes **18*a*** and the chamber **36**, removable front portions are provided in the walls of the chambers. A typical construction of the walls of each of these chambers is shown in Figure 6 which represents a cross-sectional view of the chamber 25*a* taken along the line 6—6 of Figure 4. The removable front wall portion 45 is affixed to the apparatus wall 10*a* by means of the bolts 47. Similar removable wall portions are provided in chambers 27*a* and 36.

During the operation of the apparatus shown in Figs. 4 and 5, the soluble substances are caused to diffuse from the layer of dialyzate which passes in the space between the tubes 18*a* and 18*b* into the diffusate which is flowing through the interior of the tube 18*a*. Simultaneously, water or solvent from the diffusate will be flowing through the tube 18*a* into the dialyzate thus diluting the dialyzate. If the procedure of dilution is not retarded, it will result in the slowing down of the process of dialysis, the rate of which depends upon the difference in concentration of the soluble material between the dialyzate and the diffusate. Thus, according to one embodiment of the present invention, air is blown over the outside of the multiwalled tube so that water is continuously evaporated from the diffusate through the wall 18*b* and through the open mesh fabric 18*c*. It has been found, for example, that when the tube 18*b* is formed of regenerated cellulose and the diffusate is an aqueous solvent, the rate of evaporation of water through the regenerated cellulose tube 18*b* is the same as the rate of evaporation from the same solution contained in a bath. In other words, the rate of evaporation appears to be independent of the membranes. This appears to be due to the fact that the water diffuses in the wall of the tube 18*b* and evaporates from its external surface. Thus, the present invention provides a process and apparatus by which the dialysis can be carried out simultaneously with the concentration of the dialyzate so that the decrease in the rate of dialysis resulting from dilution of the diffusate can be substantially retarded or prevented. Preferably, the air which is caused to flow over the tube 18*c* is air heated to an elevated temperature of the boiling point of water, but preferably between 50 and 60° F. The heat transferred to the dialyzate is thus advantageous in preventing further fermentation and increasing the rate of dialysis. Any conventional air blower and air heater may be employed.

For treating aqueous liquid compositions, the tubes 18, 18*a* and 18*b* may be formed of any hydrophilic film-forming material, such, for example, as parchment paper, tubes made from leather waste as sold under the trade names "Brechteen" and "Naturin" and tubes made from any film-forming non-fibrous cellulosic materials as a class. For the treatment of aqueous fluid compositions where it is desired to cause the diffusion and separation of water or water-miscible organic compounds from inorganic or organic substances whether liquid or solids, there is preferably employed a hydrophilic cellulosic tube such, for example, as one formed of regenerated cellulose or cellulose hydrate which has been produced by regeneration from viscose or from solutions of cellulose in inorganic or organic solvents or from cuprammonium cellulose or by the deesterification of cellulose esters such as by the denitration of cellulose nitrate, also membranes formed of alkali-soluble, water-insoluble cellulose ethers, gelatine (insolubilized), casein, alginates, and the like film-forming hydrophilic plastic materials. Such tubes are employed in

the wet gel state, i. e., while they are swollen with water.

On the other hand, when it is desired to separate a hydrophilic organic liquid from water or organic compounds of a different type there may be employed tubes formed of hydrophobic colloidal materials as a class of which there may be given by way of example, tubes formed of synthetic resins such as polyvinyl resins, methyl methacrylate resins, chloroprene, nylon, chlorinated rubber and the like, or from an organic solvent-soluble cellulose derivative such, for example, as a cellulose ester, cellulose ether, mixed cellulose ester, mixed cellulose ether, a mixed ether ester of cellulose, as well as tubes formed of two or more resins or two or more cellulose derivatives, also tubes formed from a mixture of a hydrophobic resin with a hydrophobic cellulose derivative. When hydrophobic tubes are employed they are preferably used in the swollen gel state, i. e., while they are saturated with the organic liquid which it is desired to evaporate through the tube.

The present apparatus is adapted for dialyzing both organic and inorganic substances from organic or aqueous solutions. On the one hand, organic substances may be separated from aqueous or non-aqueous organic solutions by use of a semi-permeable hydrophobic tubing, while on the other hand water-soluble substances may be separated from aqueous solutions by use of a hydrophilic tubing. Accordingly, the present apparatus may be used for separating inorganic or organic crystalloids from their solutions, or for separating crystalloids from colloids, or for separating inorganic substances from organic substances, or for separating organic liquids from aqueous or non-aqueous solutions. In particular, the apparatus is applicable for the separation of glycerine, butylene glycol, citric acid, sugar and inorganic salts and the like, from their aqueous solutions.

The heating of the dialyzate from 70 to 100° C. serves a four-fold purpose: (*a*) to continuously concentrate the dialyzate since water is evaporated in the evaporator; (*b*) to increase the rate of dialysis; (*c*) to eliminate dissolved air and air bubbles; (*d*) to sterilize the dialyzate and prevent further fermentation.

The apparatus has many advantages, namely, the dialyzing membranes being in the form of a tube are more self-supporting than flat sheets and they can be readily anchored at each end without danger of leaks. When a tube breaks, the liquid may be quickly drained from the apparatus and a tube replaced without dismantling the entire apparatus. Since the tubes are not constricted at the entrance or exit where they are joined to the headers, the flow of liquid therethrough is not retarded and there is no tendency for sediment to collect inside the tube; further, a rapid flow can be maintained through the tubes. Thus, there is provided a means for continuously concentrating the dialyzate while preventing the rate of dialysis from dropping too rapidly, thereby resulting in an increase in the yield.

Since certain changes in carrying out the above process and in the constructions set forth, which embody the invention, may be made without departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. An apparatus for the dialysis of solutions comprising, in combination, a chamber, a multiplicity of tubular dialyzing membranes comprising outer tubes of relatively large diameter and tubes of relatively small diameter disposed in said tubes of large diameter, means spaced within said chamber supporting said tubular dialyzing membranes, means to pass the solution to be dialyzed through the outer tube into contact with one surface of the inner tube, means to pass another liquid through the inner tube into contact with the other surface of the inner tube, and means to continuously concentrate the solution being dialyzed so as to increase the rate of dialysis.

2. An apparatus for the dialysis of solutions comprising, in combination, a chamber, a multiplicity of tubular dialyzing membranes, comprising outer tubes of relatively large diameter and tubes of relatively small diameter disposed in said tubes of large diameter having tubular support for the outer tube comprising an open mesh fabric, disposed therein, means spaced within said chamber supporting said tubular dialyzing membranes, means to pass the solution to be dialyzed through the outer tube into contact with one surface of the inner tube, means to pass another liquid into contact with the other surface of the inner tube, and means to continuously concentrate the solution being dialyzed so as to increase the rate of dialysis.

3. An apparatus for the dialysis of solutions comprising, in combination, a chamber having inner and outer headers disposed transversely adjacent each end and defining a space between them, dialyzing membranes in the form of inner and outer concentric tubes of different diameters disposed in said space and connected at each end to said headers, the inner tube being connected to the outer headers and the outer tube being connected to the inner headers, means to pass a solution through the inner tube, means to pass a different solution through the space between the inner and the outer tube, and means to pass a fluid on the outside of the outer tube.

4. An apparatus according to claim 3 in which there is provided means for passing air over the surface of the outer dialyzer tube so as to evaporate liquid from the surface of said tube.

5. A process for the dialysis of solutions comprising passing the solution to be dialyzed into contact with one surface of a dialyzing membrane in the form of a tube, passing another liquid into contact with the other surface of said tube, and continuously concentrating the solution being dialyzed at a point spaced from the dialyzing membrane, and continuously recirculating the concentrated solution, whereby the concentration gradient between the dialyzate and the diffusate is maintained at its highest level throughout the dialysis process.

6. A process for dialyzing solutions comprising passing the solution to be dialyzed through an outer tubular dialyzer, in contact with an inner tubular dialyzer which is concentric with the first tubular dialyzer, passing another liquid through and in contact with the inner tubular dialyzer, and passing air over the external surface of the outer tubular dialyzer whereby a liquid is caused to be evaporated from said dialyzer.

7. A process for dialyzing solutions comprising passing the solution to be dialyzed through a tubular dialyzer of relatively large diameter in contact with tubular dialyzer of smaller diameter which is disposed inside said larger tubular dialyzer, passing another liquid through and in contact with the tubular dialyzer of smaller diameter, and passing a third fluid over the external surface of the larger tubular dialyzer.

JUSTIN ZENDER.

Nov. 19, 1946.

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2,411,239

APPARATUS FOR DIALYZING

Filed July 8, 1943

2 Sheets-Sheet 1

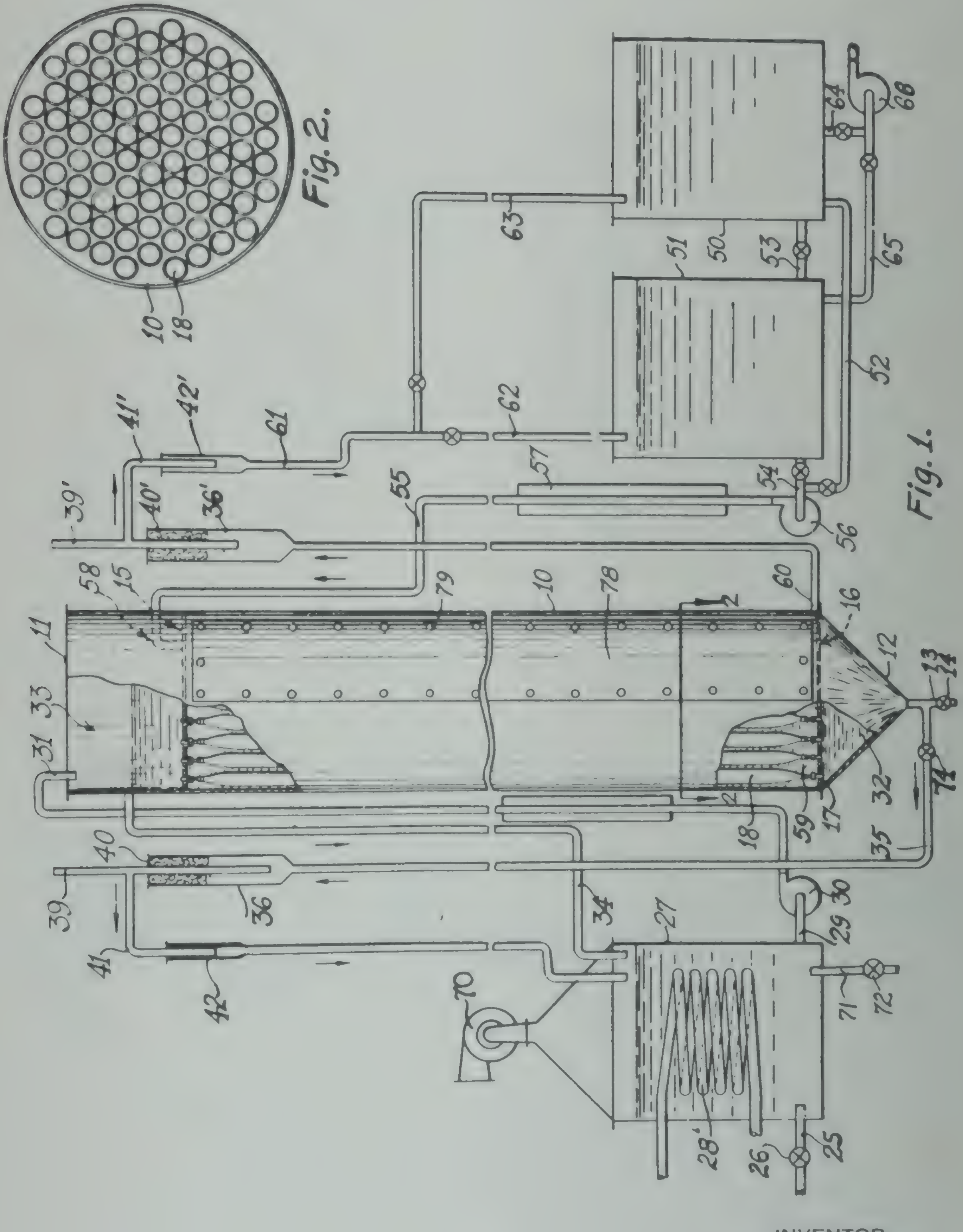

Fig. 2.

Fig. 1.

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APPARATUS FOR DIALYZING

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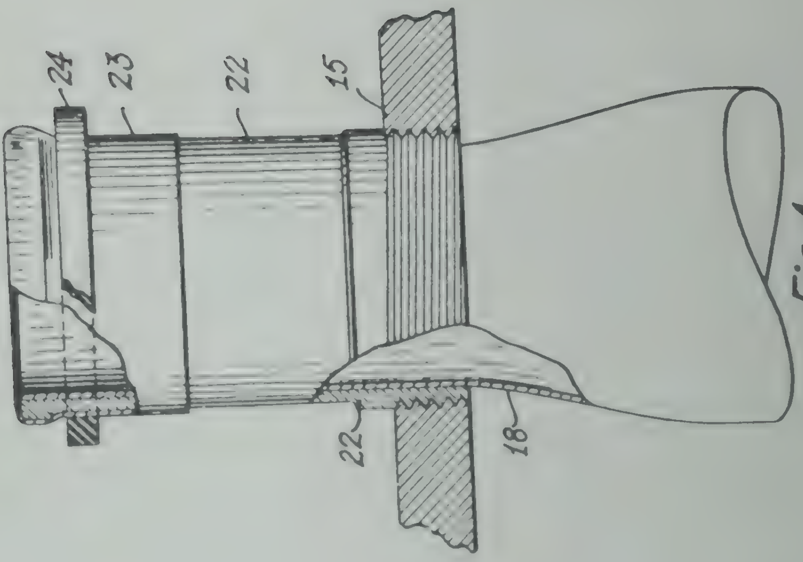

Fig. 4.

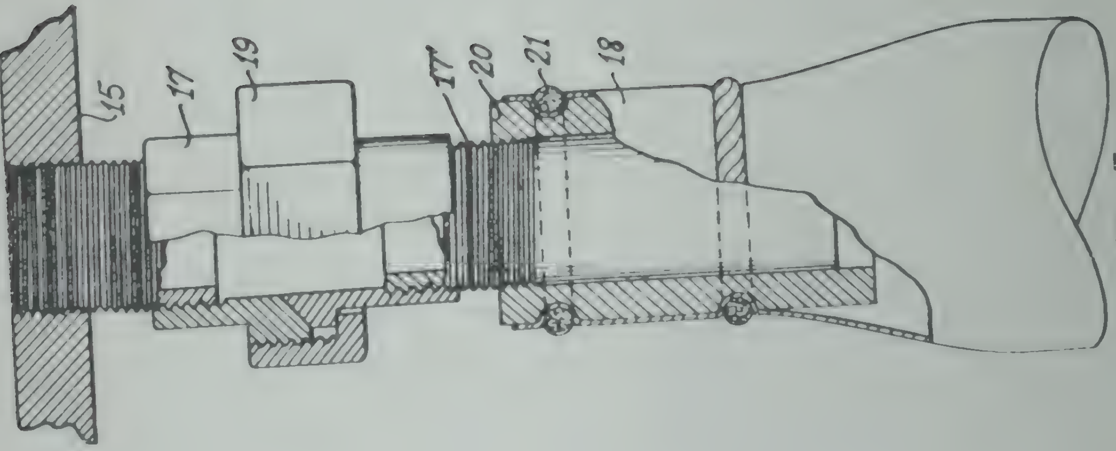

Fig. 3.

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APPARATUS FOR DIALYZING

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6 Claims. (Cl. 210—8.5)

The invention relates in general to dialysis, and, in particular, to an apparatus for the separation of a soluble substance from its solution by dialysis, and to correlated improvements designed to enhance the structure and function and to extend the uses of such apparatus.

It has been proposed to dialyze soluble materials from their aqueous solutions through hydrophilic membranes, such, for example, as sheets of regenerated cellulose, parchment paper, and the like. However, dialyzers employing membranes in the form of flat sheets have certain inherent disadvantages. For example, the edges of the sheets must be maintained under pressure or firmly sealed to avoid loss of liquid during dialysis. To clean the apparatus or to replace a broken sheet it is generally necessary to completely dismantle the dialyzer. Further, to decrease breakage, the membranes must be supported over their surfaces. Finally, such prior apparatus did not provide any means for retarding the dilution of the solution being dialyzed. Thus, sheet dialyzers of prior design have generally been complicated in construction, difficult to repair or to clean and capable of handling only small volumes of liquid.

Accordingly, it is a general object of the present invention to provide a dialyzer which will be capable of handling large volumes of liquid and which will operate rapidly.

It is a further general object to provide a dialyzing apparatus which is easy to construct and to clean and in which broken membranes may be replaced without completely dismantling the dialyzer.

A specific object is to provide an apparatus for means of retarding the dilution of the solution being dialyzed.

Other objects of the invention will in part be obvious, and will in part appear hereinafter.

According to the present invention, there is provided an apparatus for the dialysis of solutions comprising in combination a chamber, a dialyzing membrane in the form of a tube disposed therein, means to pass the solution to be dialyzed into contact with one surface of the tube, means to pass another liquid into contact with the other surface of the tube, means to heat the solution being dialyzed and/or the other liquid, and preferably means to maintain a pressure differential between the inside and the outside of the tube to distend the tube.

In the following specifications and in the appended claims, the term "dialyzate" will be used to designate the solution being dialyzed in accordance with recent usage in the art; the term "diffusate" will designate the solution of the material which diffuses through the membrane during dialysis, and the term "dialysis" will be used to designate the diffusion of soluble substances through a semi-permeable membrane from one liquid into another.

The invention accordingly comprises the features of construction, combinations of elements, and arrangement of parts which will be exemplified in the construction hereinafter set forth and the scope of the invention will be indicated in the claims.

For a more complete understanding of the nature and objects of the invention, reference should be had to the accompanying drawings in which Figure 1 represents a side elevation of one embodiment of the apparatus of the invention, and Figure 2 represents a cross-sectional view of the dialysis chamber of the apparatus of Figure 1 taken along the line **2—2** thereof. Figures 3 and 4 show two embodiments of means for anchoring the dialyzing tubes to the headers of the apparatus shown in Figure 1.

In that embodiment of the apparatus shown in Figs. 1 and 2, the dialyzing chamber proper comprises a vertical outer chamber **10**, which is shown as a cylindrical chamber, but which may be of any cross-sectional shape. The chamber is closed at the top by a plate **11**, and is closed at the bottom by a conical base **12**, which is provided with a drain **13** having a valve **14**. Situated adjacent the ends inside the chamber **10**, there are positioned headers **15** and **16**, each provided with a plurality of holes into which are threaded short sections of pipe **17**, which serve to anchor the dialysis tubes **18** to the headers.

The chamber **10** is provided with a removable side portion **78** attached to the tank by the bolts **79** so as to make the dialysis tubes **18** accessible from the outside. When a tube bursts, it is thus possible to reach it and insert a new tube. To change a tube, particularly where it is in the center or opposite side of the chamber, it is desirable to drain the apparatus. The empty tubes obstructing the way may then be collapsed and pushed to one side to a sufficient extent to insert the new tube in its proper location. In order to insert a new tube, it is therefore not necessary, in general, to remove the tube located between the opening into the chamber and the tube to be replaced.

The anchoring or sealing of the dialysis tubes to the headers may be effected by any suitable means, but there is shown in Figs. 3 and 4 two means found suitable for this purpose. Referring to Fig. 3, the numeral **15** represents the upper header into which is screwed a short section of pipe **17** having a threaded union joint **19**, the lower end of the pipe **17′** being sealed by means of a tubular sleeve **20** formed of a resilient material, such, for example as rubber, cork, sponge, or the like, which forms a soft cushion to support the dialysis tube **18**, which is slipped over the sleeve and fixed thereto by means of the cords **21**. If desired, the outer surface of the sleeve **18** may be grooved to provide seats for the cord **21**. The lower end of the dialysis tube **18** may be united to the lower header by similar means as shown in Fig. 3. The joint shown in Fig. 3 is particularly advantageous when the chamber is being fitted with the tubes initially or when a dialysis tube is being replaced after breakage because, in this case, the disconnection of the lower section of the pipe **17** from the upper section, and the mounting of the tube **18** on the sleeve **20** can take place outside of the chamber **10**, after which the ends are joined to the headers by means of the threaded joint **19**.

An alternative means of anchoring the dialysis tubes to the headers is illustrated in Fig. 4, in which embodiment the header **15** is provided with a threaded section of pipe **22**. The casing is pulled through the section of the pipe and the end turned down over the upper end of the pipe **22** to form the cuff **23** which may be anchored to the pipe by means of the band **24**, which may be formed of rubber as shown, or of metal or the like. The tube **18** may be mounted on the lower header **16** by means similar to that shown in Fig. 4. The coupling shown in Fig. 4 has the advantage of maintaining the maximum diameter of the tube **18** at the joint, and thus does not interfere with the flow of the liquid through the tube **18**.

The dialysis tubes **18** may be disposed and arranged within the chamber **10** in any desired manner, in rows, for example, as shown in Fig. 2 or in concentric circles. The space between the tubes can be varied as desired, but in general a distance of the order of ½ to 1 inch is sufficient. It is to be understood that a space exists around all of the tubes illustrated in Fig. 2, and that none of these tubes are in direct contact with each other along their longitudinal surfaces.

It may be understood that the apparatus shown in Fig. 1 may be constructed and arranged that the dialyzate may be caused to pass inside the tubes or outside the tubes, but for the purpose of illustration only, the apparatus of Fig. 1 is shown constructed so that the dialyzate will pass through the interior of the tube **18**. The liquid to be dialyzed, that is, the dialyzate, may be taken from a suitable reservoir and fed through the pipe **25** having a valve **26** into an evaporator **27**. The liquid in the evaporator may be heated from 30° to 100° C., preferably above 70° C., by conventional means and/or suction may be applied through the pump **70** to draw off water, alcohol and other volatile substances from the dialyzate. Heating and suction also facilitate elimination of bubbles from the dialyzate, the presence of which tends to favor the growth of organisms which attack the dialyzing membranes. The evaporator can be drained for cleaning by opening the outlet pipe **71** by means of valve **72**. From the evaporator, the dialyzate passes through the pipe **29** by means of the pump **30**, and is then heated by

means of the heater **28** and introduced into the chamber **10** through the inlet **31**. The dialyzate fills the lower space **32** of the chamber, the tubes **18**, and the upper space **33** until the level is such that the dialyzate overflows through the drain **34** which returns the excess to the evaporator **27**.

During operation, the dialyzate is preferably continuously circulated. Therefore, there is provided an outlet pipe **35** equipped with a valve **74** which is positioned at the base of the conical bottom **12**. The pipe **35** is disposed vertically and has attached to its upper end an enlarged section **36** into which is disposed an extension tube **39** sliding through a hole provided in the packing **40**. Between the ends of the tube **39**, a branch **41** carries the solution into a pipe **42** which is attached to the upper end and surrounds the lower end of the pipe **41** which slides therein. Pipe **42** discharges the dialyzate into the evaporator **27**. By raising or lowering the pipe **39**, it is possible to assure that the level of the dialyzate in the chamber **33** will be at all times above the header **15**, and if necessary, up to the level of the overflow pipe **34**. By this means, one can insure that the dialyzing tubes will be completely filled with the dialyzate even though the dialyzate is being circulated downward through these tubes.

The apparatus also includes means for bringing a liquid into contact with the outside of the dialyzing tubes **18**. These means comprise storage tanks **50** and **51** from which liquid may be removed by means of pipes **52**, **53**, and **54**, each of which is provided with a suitable valve, the liquid being forced upward through the pipe **55** by means of the pump **56** and heated if desired by means of the cylindrical heater **57**. The pipe **55** provides means for entering the chamber **10** at a point above the upper header and then communicates with the space between the headers by passing through the plate **15** as shown by the broken lines **58**. The diffusate flows downward and around the tubes **18** until it fills completely the space **59** between the headers **15** and **16**. The excess liquid is removed from the lower end of the space **59** through pipe **60**, which has an enlarged upper end **36′**, an extension **39′** passing through the packing **40′**, the extension **39′** having a branch **41′** which discharges the liquid into a funnel **42′** which is fixed into the upper end of the drain **61**. From pipe **61** the diffusate may be passed through the pipe **62** to the reservoir **51** or through the pipe **63** to the reservoir **50**. The diffusate may be discharged from the reservoir **50** through the pipe **64** or from the reservoir **51** through the pipe **65** and forced by means of the pump **66** to storage or point of use.

While the apparatus shown in Fig. 1 is constructed so that both the dialyzate and the diffusate flow concurrently and downward in the chamber **10**, it is to be understood that the apparatus can be modified without transcending the scope of the present invention so as to provide that the dialyzate and the diffusate flow upward or flow countercurrent to each other.

Further, the apparatus may be readily modified by anyone skilled in the art, without transcending the scope of the present invention so that the chamber **10** and the tubes **18** are disposed in a horizontal plane. Inasmuch as the tubes **18** during operation are not only completely filled with liquid but also are completely surrounded by liquid, the tubes will require little or no horizontal support. If the tubes **18** are filled with dialyzate, which has a higher specific gravity than the diffusate, the tubes will tend to float so that they can be kept in position merely by suitable guide pins.

During the process of dialysis, water from the diffusate continuously diffuses into the more concentrated dialyzate, thus diluting the dialyzate and slowing down the process of dialysis. In order to avoid this decrease in the rate of diffusion resulting from dialysis, the present apparatus provides an evaporator **27** in which the dialyzate may be heated by means of the steam coil **28′**. The top of the tank **27** is left open to permit evaporation of water from the dialyzate. By this means, the dialyzate may be continually concentrated while it is being circulated and subjected to dialysis. Moreover, the heating of the dialyzate serves the purpose of evaporating water or other volatile liquids from the dialyzate thus maintaining the concentration and viscosity of this liquid. The temperature of the dialyzate may be kept above the temperature at which the fermentation or bacterial decomposition occurs, thus avoiding changes in composition or loss of desired material through fermentation.

The present apparatus is adapted for dialyzing both organic and inorganic substances from organic or aqueous solutions. Organic substances may be separated from solutions by use of a semipermeable hydrophobic tubing. For the dialysis of aqueous solutions, a hydrophilic tubing is employed. Accordingly, the present apparatus may be used for separating inorganic or organic crystalloids from their solutions, or for separating crystalloids from colloids, or for separating inorganic liquids from organic liquids, or for separating organic liquids from aqueous or nonaqueous solutions. In particular, the apparatus is applicable for the separation of glycerine, butylene glycol, and citric acid, sugar and inorganic salts from their aqueous solutions.

The heating of the dialyzate from 70°–100° C. serves a four-fold purpose: (*a*) to continuously concentrate the dialyzate since water is evaporated in the evaporator; (*b*) to increase the rate of dialysis; (*c*) to eliminate dissolved air and air bubbles; (*d*) to sterilize the dialyzate and prevent further fermentation.

The apparatus has many advantages, namely, the dialyzing membranes being in the form of a tube are more self-supporting than flat sheets and they can be readily anchored at each end without danger of leaks. When a tube breaks, the liquid may be quickly drained from the apparatus and a tube replaced without dismantling the entire apparatus. Since the tubes are not constricted at the entrance or exit where they are joined to the headers, the flow of liquid therethrough is not retarded and there is no tendency for sediment to collect inside the tube; further, a rapid flow can be maintained through the tubes. Thus, there is provided a means for continuously concentrating the dialyzate while preventing the rate of dialysis from dropping too rapidly, thereby resulting in an increase in the yield.

Since certain changes may be made in the above construction and different embodiments of the invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An apparatus for the dialysis of liquid solutions comprising, in combination, a chamber, means of dialysis comprising a dialyzing membrane in the form of a tube disposed therein, means for continuously circulating the solution to be dialyzed in contact with one surface of the tube, means for passing another liquid into contact with the other surface of the tube, means for concentrating the dialyzate after passage through the dialyzing tube, and means for recirculating the concentrated dialyzate through the tube.

2. An apparatus for the dialysis of liquid solutions comprising, in combination, a chamber, means of dialysis comprising a dialyzing membrane in the form of a tube disposed therein, means for continuously circulating the solution to be dialyzed in contact with one surface of the tube, means for passing another liquid into contact with the other surface of the tube, means for concentrating the dialyzate after passage through the dialyzing tube, means for recirculating the concentrated dialyzate through the tube, and means for maintaining a hydrostatic pressure differential between the inside and outside of said tube to distend the tube.

3. An apparatus for the dialysis of liquid solutions comprising, in combination, a chamber, headers disposed transversely adjacent each end of said chamber so as to divide said chamber into a middle and two end compartments, a plurality of tubular dialyzing membranes disposed between said headers and communicating with the end compartments, means for continuously circulating a solution through the end compartments and through said dialyzing tubes means for withdrawing said solution from said tubes, means for passing another liquid through said middle compartment into contact with the exterior of said dialyzing tubes and means for withdrawing said liquid from said compartment.

4. An apparatus according to claim 3 in which the tubes are affixed to the headers by means of a threaded union joint so that said tubes are separately removable.

5. An apparatus according to claim 3 in which there is provided means for concentrating one of said liquids positioned outside of said chamber.

6. An apparatus according to claim 3 in which there is provided means for heating at least one of said liquids.

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PROCESS FOR THE CLARIFICATION OF FERMENTED LIQUORS

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1 Claim. (Cl. 260—637)

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The invention relates in general to the purification of fermented liquors, and in particular to a process for the purification of glycerol solutions produced by fermentation.

The process of the present invention is applicable for the purification of various fermented liquors but, for purposes of illustration only, the process will be described with respect to the purification of glycerol solutions produced by fermentation. While glycerol solutions of high clarity and free from impurities may be produced by the fermentation of colorless sugar solutions, molasses is a more economical source of sugar for this purpose. However, the fermentation of molasses solutions always results in a fermented liquor which contains a wide variety of impurities and by-products and has a pronounced dark color. The byproducts include volatile substances such as alcohol, acetone, acetic acid, and the like, while the impurities comprise pectins, unfermented sugar, cellulose, natural gums and resins, inorganic salts, especially salts of alkaline earth metals and iron and sulphates. The color of the solution obtained by the fermentation of molasses is due in part to organic colloids and in part to the presence of iron. It is apparent that the recovery of a substantially pure and colorless solution of glycerine from such a complex system involves numerous difficulties.

Heretofore it has been suggested to remove the water and volatile organic compounds from the fermented liquor by evaporation, and to separate the water-soluble compounds from the organic colloids by dialysis as through a semi-permeable membrane formed by regenerated cellulose. However, the diffusate obtained by such dialysis still has a dark brown color which is objectionable when the glycerol is to be used as a softening agent for transparent materials, paper, and in cosmetics, pharmaceuticals, and plastics.

Accordingly, it is generally the object of the present invention to provide a method for the production of substantially clear and colorless solutions from fermentation liquors.

It is a specific object of the present invention to provide a process for the recovery of a substantially clear and colorless solution of glycerol from the liquor produced by the fermentation of molasses.

It is a further specific object to remove from fermentation glycerol solutions such inorganic impurities as calcium, iron, and sulphates.

It is another specific object to reduce the color of glycerol solutions produced by fermentation

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so that the solution is adapted for use as a softening agent for transparent sheeting and in pharmaceuticals.

Further objects of the invention will in part be obvious and will in part appear hereinafter.

According to the present invention there is provided a process for the purification of fermented liquors including the steps of treating a fermented liquor to precipitate iron as iron sulfide, dialyzing the liquor, treating the liquor to precipitate sulphates therefrom, treating the resulting liquor to precipitate alkaline earth metals therefrom, and decolorizing the liquor by contacting it with an absorbent material. In the preferred embodiment these steps are carried out in the following sequence: treating the fermented liquor to precipitate iron as iron sulfide, dialyzing the treated liquor, treating the diffusate to precipitate sulphates therefrom, thereafter treating the resulting liquor to precipitate alkaline earth metals therefrom, and decolorizing the filtrate with an absorbent material. After such clarification the clarified liquid may be filtered and concentrated if desired.

The invention accordingly comprises a process having the steps and relation of steps one to another all as set forth in the following detailed description and the scope of the application of which will be indicated in the claim.

The present process is adapted for the clarification of fermented liquors of all types but it is especially adapted for the clarification of liquors resulting from the fermentation of carbohydrates, this term being used to include cellulose, starches and sugars. Thus, the present process may be used for the purification of fermented liquors resulting from the production of such substances as glycerol, the glycols, in particular 2-3-butylene glycol, higher alcohols, polyhydric alcohols, and various organic acids, such, for example, as citric, lactic, fumaric, tartaric, oxalic, and the like. In the production of such substances by fermentation of natural occurring carbohydrates, the fermented liquor will contain a wide variety of by-products and impurities and has a pronounced dark color. The byproducts frequently include volatile substances, such as alcohol, acetone, acetic acid and the like, while the impurities usually comprise pectins, unfermented sugar, cellulose, natural gums, and inorganic salts, especially salts of alkaline earth metals and of iron; and also substantial quantities of sulphates. The dark color of a liquor resulting from the fermentation of a natural-occurring carbohydrate is due in part to the organic colloids present and in part to the presence of iron. The present invention provides a process for the production of substantially pure and colorless solutions from such fermented liquors.

In the following detailed description a process will be described with reference to the purification of glycerine solutions obtained by fermentation of molasses, but it is to be understood that the invention is not limited to the purification of such liquors.

In general, the fermented liquor is subjected to certain preliminary treatments prior to being subjected to the essential purifying and clarifying steps of the present process. Normally, it will be desirable to evaporate from the liquor the volatile organic substances, such as alcohol, acetone, acetic acid, and the like. This is normally carried out by distillation in copper stills. Since ammonia is frequently produced during such distillation, it is customary to acidify the fermenting liquor and to maintain it acid during the distillation. Therefore the residue, after distillation, should be neutralized with any suitable alkaline compound, such, for example, as lime, sodium hydroxide, potassium bicarbonate, and the like and then concentrated until the liquor is concentrated to about 50% of its volume. Such concentration reduces the volume of liquid to be treated by the subsequent purification process. The fermented liquor, after such concentration, is heated and there is added an aqueous solution of a water-soluble sulfide such as ammonium, sodium, potassium, calcium and strontium sulfides, hydrogen sulfide, and the like, in sufficient concentration to precipitate the iron as ferrous sulfide. The iron appears to be one of the chief causes of the dark color of the solution. The removal of the iron prior to the step of dialysis eliminates subsequent filtration.

After precipitation of the iron, the solution is dialyzed through a semi-permeable membrane, the precipitated iron sulfide being retained by the membrane. For the dialysis membrane there may be employed parchment paper or a hydrophilic pellicle, such, for example, as regenerated cellulose produced from viscose or by the denitration of nitrocellulose, or from cuprammonia solutions of cellulose. In the now preferred embodiment the dialysis membrane is a tube of regenerated cellulose. The process of dialysis may be carried out in the apparatus and according to the procedure described in the copending applications Serial Nos. 493,918, now Patent No. 2,411,238, Nov. 19, 1946, and 493,919, now Patent No. 2,411,239, Nov. 19, 1946, both filed July 8, 1943.

By the dialysis the glycerol and other water-soluble substances are separated from the organic colloids. The diffusate thus obtained is next treated to remove sulfate ion, with an aqueous solution of a water-soluble salt of an alkaline earth metal such, for example, as calcium, barium, strontium chlorides, acetates, nitrates, and the like, to precipitate the sulphates of the alkaline earth metal. Before filtering, the diffusate is first acidified, as with acetic acid, and then treated with a water-soluble salt which will cause the precipitation of the alkaline earth metal. Suitable salts are carbonates, oxalates, orthophosphates and tartrates of ammonium, potassium, sodium, and lithium.

The solution thus obtained is filtered and the filtrate is treated to remove color with activated carbon silica gel or other absorbent for a period of about one hour at an elevated temperature. For example, with activated carbon, the treatment is carried out at a temperature from 40 to 100° C., preferably 80° C., while the solution is slightly acid. The activated carbon appears to remove most of the residual color due to organic substances. The clarified solution thus obtained is filtered to recover the spent carbon. The spent carbon may be reactivated by heating in a conventional manner and then reused.

The filtrate thus obtained is neutralized, then passed in vacuum evaporators in which the solution may be concentrated as desired. The solution is neutralized by use of a dilute solution of a water-soluble alkaline compound such, for example, as the hydroxides, carbonates and acetates of the alkali metals, or by ammonia. The concentration of the clarified solution must be carried out under vacuum and at a relatively low temperature to prevent any additional discoloration which results when the solution is heated to the boiling point at atmospheric pressure. After the concentrated solution is allowed to stand or cools down, salts, such as potassium sulfate and potassium chloride, precipitate and may be removed by filtration. The separated salts are allowed to settle and the solution decanted and filtered if necessary.

The solution thus obtained is substantially free of iron and alkaline earth metal salts and of sulphates. It is characterized by being substantially clear and colorless, depending upon the extent of decolorizing. The glycerine solution thus obtained is sufficiently clear and colorless to be employed as a softening agent for transparent materials such as Cellophane, gelatin, casein and papers of all kinds, including glassine paper, leather, cosmetics and pharmaceuticals, and in the manufacture of synthetic resins.

By way of illustration but not by way of limiting the invention, there will be given the following specific example:

A liquor resulting from the fermentation of molasses in an alkaline medium for the production of glycerol is rendered slightly acid and the alcohol and acetone distilled off in a copper still. The residue is then concentrated to about 50% of its initial volume and then neutralized with a 10% aqueous solution of potassium bicarbonate. The concentrated liquid is then heated and there is added, with stirring, a 20% aqueous solution of calcium sulfide which precipitates the iron as iron sulfide. Without filtering the solution, the liquid is decanted from the precipitate and dialyzed with water through a regenerated cellulose tube in a multitube dialyzer according to the procedure described in the co-pending application Serial No. 493,919, now Patent No. 2,411,239, Nov. 19, 1946, filed July 8, 1943. The diffusate is a dilute solution of glycerol having a dark brown color due to organic coloring matter. The diffusate is then treated with a 10% aqueous solution of barium acetate to precipitate sulphate ions as barium sulphate. The solution is then acidified with 10% aqueous solution of acetic acid to a pH 6 and then treated with a 10% aqueous solution of oxalic acid to precipitate barium and calcium ions as the oxalates. The solution is then filtered and the filtrate is treated with a mass of activated carbon for one hour at a temperature of 80° C., as a result of which the dark color is substantially removed. The substantially colorless solution is then filtered to remove the spent carbon which may be reactivated and reused. The filtrate is then concentrated in vacuum evaporators at room temperature. During such concentration some potassium sulphate and potassium chloride precipitates and is removed by an additional filtration.

It is to be understood that the invention is not limited to a process in which the sequence of steps is that given in the above description since it is possible, without transcending the scope of the invention to carry out the steps of the process in a different order. For example, the decolorizing of the solution by means of an absorbent material, e. g. activated carbon, can be carried out at an earlier stage in the process conveniently immediately after the dialyzing step. Since the dialyzing operation removes some of the color, it is not advantageous to decolorize prior to dialyzing. On the other hand, the precipitation of the iron and of the sulphate ions may occur in reverse order from that given.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

A process for the purification of fermented liquors comprising the steps of treating a fermented liquor with a water-soluble sulfide to precipitate iron as iron sulfide, dialyzing the liquor, treating the diffusate with a water-soluble salt of an alkaline earth metal to precipitate sulphates therefrom thereafter making the diffusate acidic and then treating the diffusate with oxalic acid to precipitate alkaline earth metals therefrom, decolorizing the diffusate by contacting it with an absorbent material, and filtering the purified diffusate.

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